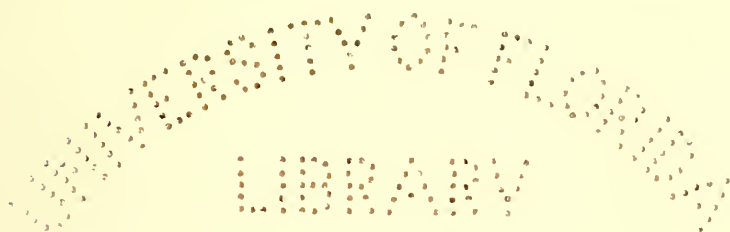# SOLUBLE SILICATES IN INDUSTRY

BY

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PHILADELPHIA QUARTZ COMPANY

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BOOK DEPARTMENT

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

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The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.
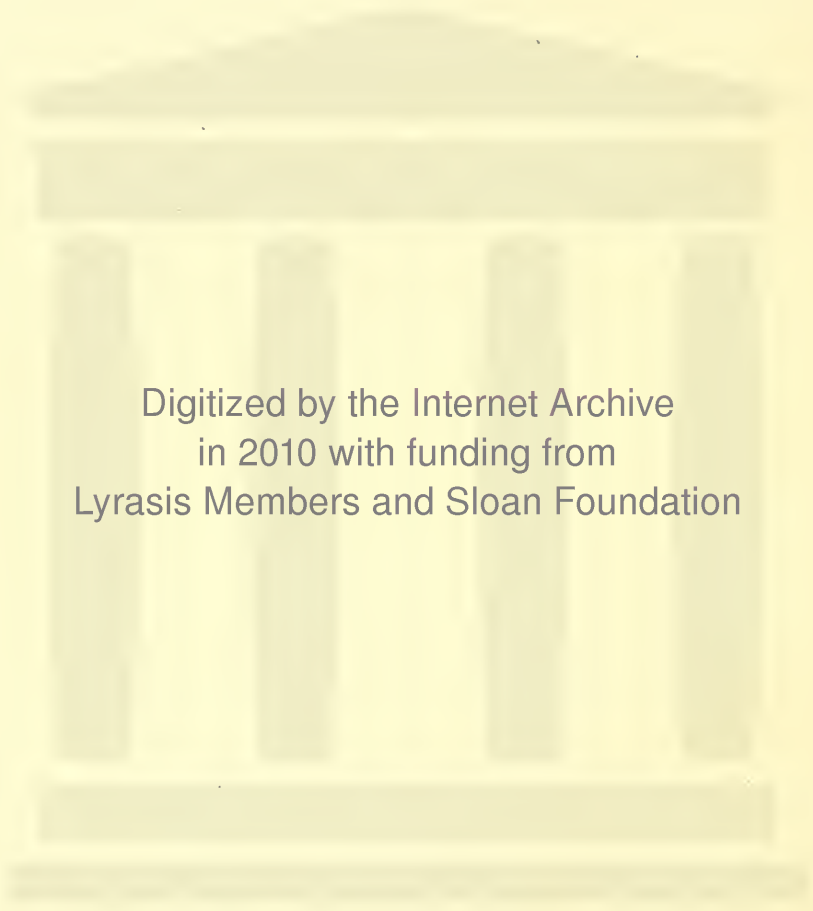
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Chapter I.

Introduction.

Historical Development.

Pliny the Elder [1] began his great book, "Naturalis Historia", with the statement that he had assembled 20,000 facts. At least as many facts pertinent to the uses of soluble silicates in industry are known, for so widely have their applications been extended in the past two decades that there are few manufacturing plants which are not using, somewhere, at least one of the many grades.

The mere assembly of facts is insufficient; there must be an effort to correlate them and to understand the reactions and properties which underlie each use separately and groups of uses collectively. The data with which to do this are in many cases incomplete, but an attempt has been made to review the most important literature and to set forth such parts of it as have been adjudged reliable and helpful for the purpose in hand. This critical selection is essential, for much has been written which is of little value in the light of our present knowledge.

Beginnings of Soluble Silicates.

Some of Pliny's accounts belong in the category of the doubtful, but one of them sets the stage for the beginnings of soluble silicates. The story [2] is of sailors who took chunks of natural soda from their cargo to support cooking vessels over their fire on a sandy beach. They were ignorant of the fact that the glass formed by the interaction of sand and soda was soluble in water. This observation was not made until many centuries later.

A manuscript accredited to the alchemist Basil Valentine and supposed to have been written about 1520, contains the first reference to

[1] Pliny, "Natural History," Text of Hardouin, Lemaire's Ed., Vol. 1 (1827), p. 16.
[2] Pliny, "Natural History," Vol. 36 (1827), p. 65-6.

soluble silicates as products of the arts.[3] He seems to have known how to make a glass which was fluid in the cold by melting a mixture of powdered silica and "sal tartari" which, after cooling, gradually became liquid on exposure to the air. It was said to be thick and oily, capable of being dried out by warming, and suitable for artificially petrifying wood or making building stone. The work, indeed the existence, of Basil Valentine is shrouded in mystery—he may be a creation of the imagination of a writer of later date; but whatever the merits of this account may be, we have reliable records beginning in the year 1640. In that year Van Helmont [4] was aware that the combination of silica with an excess of alkali will become liquid in damp places and that it is possible to precipitate silica equal in weight to the original amount by treatment of the solution with acids. Eight years later Glauber [5] named the liquid "oleum silicium" and showed that solutions of various metallic salts caused the precipitation of compounds of silicic acid and the metal. These were proposed as specifics for the treatment of gallstones. The results were not encouraging and the discovery was forgotten. Records show that Georg Bauer, often referred to as Agricola, knew of the existence of a silicate of potash.[6] In 1783 Guyton de Morveau melted quartz and sodium carbonate together; the fusion resulted in a transparent glass that could be dissolved in water.[7]

INDUSTRIAL USES.

The real beginning of industrial uses for soluble silicates was due to the work of Johann Nepomuk von Fuchs.[8] He rediscovered them by accident in 1818 in the course of experiments undertaken for the purpose of purifying silicic acid. He dissolved silica in caustic potash, observed the glass-like properties of the solution, and named it waterglass. After investigating its property of hardening when spread upon surfaces, he was able to show how it could be employed as a coating of glass for a multitude of different uses. Some of these have survived until the present time—others were based on insufficient knowledge and have been forgotten. Von Fuchs proposed soluble silicates as glues, cements and mortars, fireproof paints, hardening agents for natural and artificial stone, and as a binder for colors used in fresco painting.

[3] *Z. Oesterr. Ingenieurer,* **14**, 229 (1862).
[4] Zwick, Hermann, "Das Wasserglas," **1877**, p. 4.
[5] Glauber, "Furnis novis philosophicis," **1648**.
[6] Agricola, "De Re Metallica," trans. by Herbert Clark Hoover and Lou Henry Hoover, **1912**.
[7] Buffon, "Die naturgeschichte der minerale," trans. by Schaltenbrand, **2** (1783-5). *Chem. Ztg.,* **19**, 117-118 (1895).
[8] von Fuchs, Johann Nepomuk, *Poly. J.,* **17**, 465-481 (1825).

He also suggested their use in the laundry, both in the process of washing directly and as a constituent of the soap; in the textile industries, for sizing and for reagents in dyeing; and as a flux for soldering and welding. He even suggested silicates for fertilizer material. Though potassium silicates are doubtless effective, the justification of their use on economic grounds is open to question until they can be produced more cheaply.

The failure of early efforts to produce a uniform product allowed some processes to fall into disuse which are now well served by silicates made under close control. Fluctuations in quality and the over-enthusiastic claims of von Fuchs account for many disappointments. Public interest which was keen in 1820 had subsided to a very low ebb in 1867 when W. Gossage & Sons of Widnes, England, exhibited a soap [9] which was said to contain thirty per cent of a 20° Baumé solution of sodium silicate. It became very popular and was made at the rate of 60 tons a week. In Vienna, a silicate coconut oil soap containing eight per cent silica as silicate was made at this time by A. C. Diedecks Sohn.[10]

In France silicate solutions became popular for making rigid surgical bandages. During the year of 1873, this use consumed 2223 kilograms.

Manufacture.

The manufacture of soluble silicates in this country dates back to 1864 when it was introduced by the Philadelphia Quartz Company. A closing of the commerce in pine products between northern manufacturers and southern harvesters, brought on by the war between the States, had forced soap into the class of a luxury because of the high cost of the rosin used in its production. It was an outgrowth of this lack that soluble silicates were first manufactured here. They were used as substitutes for rosin.

Other uses developed steadily, though until the opening of the present century the increase of tonnage was very slow. Mostly, the new uses were based on the old suggestions; but as interest increased, fresh ideas evolved and developments are perhaps more actively in progress now than at any former time.

Literature of the Silicates.

There are comparatively few general treatises on waterglass although it is referred to in practically every work on general chemistry. Von

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[9] *Oesterr. Ausstellungsber.*, **5**, 438 (1867).
[10] Zwick, Hermann, "Das Wasserglas," **1877**, p. 10.

Fuchs published his researches in 1825. A forty-six page pamphlet by Zwick [11] in 1877 gives a good statement of the available knowledge of soluble silicates in Germany at that time and Krätzer [12] in 1887 published a book which, even in revised editions of 1907 and 1922, is much out of date. A book by Bernhard [13] was published in 1893; Dralle devoted a section of his work on glass making to soluble silicates (1911) and Mayer [14] published a useful but brief treatise in 1925. The rest of the literature is scattered as journal articles and incidental treatments in books on other subjects or works of reference. The Carnegie Library of Pittsburgh [15] published in 1922 a valuable bibliography, but a daily contact with problems related to soluble silicates emphasizes the fact that there is much known which has never been published and critical treatment from the point of view of American industry is lacking.

NOMENCLATURE.

The nomenclature of silicates throughout the literature is various. The word silicate of soda is so deeply intrenched in commercial usage that it seemed best not to set it entirely aside. In writing formulas, the practice is here adopted of using the symbols for the two oxides with a period between them when it is intended to indicate a definite compound. A comma has been used between the two oxide symbols when the purpose of the formula is merely to indicate the ratio in which oxides are present. Sodium disilicate will thus be represented as $Na_2O.2SiO_2$, while a system of the same ultimate composition in which the state of chemical combination is not known will be represented as $Na_2O, 2SiO_2$.

PRESENT IMPORTANCE.

The present scope of the industry in the United States [16] may be gauged by the following statistics taken from a report by the Bureau of the Census. The weights are based on 40° Baumé liquid which contains about 38 per cent total solids. The result is approximate only as

[11] Zwick, *op. cit.*
[12] Krätzer, Hermann, "Wasserglas und Infusorienerde," Hartleben's "chemisch-technische Bibliothek," 1907.
[13] Bernhard, L., "Das Wasserglas," 1893.
[14] Mayer, Hermann, "Das Wasserglas," Sammlung Vieweg, No. 79, Friedr. Vieweg & Sohn Akt.-ges. Braunschweig, 1925.
[15] Carnegie Library of Pittsburgh, "Waterglass, A Bibliography," compiled by Morris Schrero, 1922.
[16] *Chem. Met. Eng.*, 34, 585 (1927).

no allowance is made for varying ratio between silica and soda, and some variation in water content.

	1925		1923
Establishments	22		21
Production	494,000	tons (2000 lbs.)	418,849
Consumed by maker.............	100,000		87,849
For sale	394,000		331,000
Value	$5,715,026		$5,066,719
Per ton	$14.48		$20.95

The 1927 production may be roundly estimated at 500,000 tons.

The other principal producing countries are England, Germany, France, Holland, Belgium, Switzerland, Italy and Greece, with relatively minor output in Mexico and Japan. Statistics are not available but a rough idea may be had by estimating production outside the United States in 1927 at 150,000 metric tons 40° Baumé solution. The necessity of establishing large units for economical production and the restriction of markets by freight costs which draw a line around each producing unit have led to a capacity far in excess of the 1927 market, not only as a whole but in each local consuming center. This is a world situation and would probably take care of a growth of 50 per cent.

From the point of view of industry, the soluble silicates are those of sodium and potassium although all the alkali metals form silicates which dissolve in water, and even ammonia affects the solubility of silica. Because of their lower cost, the sodium compounds are used in amounts compared with which those of potassium silicates are insignificant. There are, however, a few cases where the distinctive advantages of potassium silicates give them a place. The following pages will therefore treat principally of sodium silicates and refer to the others primarily for the purpose of analogy and suggestion.

Silicates of soda provide a favorite theme for the patentee. In particular, that type of inventor who produces compositions of matter without competent knowledge of the materials he uses, seems to find much of interest in the colloidal and fire-resisting properties of the commercial grades. Their low cost is doubtless an added attraction. Numerous patent citations will be found in the following pages, but it should be understood that no attempt has been made to treat this literature exhaustively nor to mention all of the hundreds of patents which have been examined but are regarded as unimportant.

Among persons interested in silicates of soda are found those whose primary outlook is based on the consideration of scientific data while there are others, perhaps a more numerous class, who think of silicates

first from a practical standpoint. To the latter, the author would suggest that they proceed next to Chapter VI, returning to Chapters II, III, IV and V later or as the data they contain may be needed for reference purposes.

Chapter II.

The Constitution of Silicate Solutions.

Natural Occurrence of Colloidal Silica.

Industrial silicate solutions are systems in which colloidal silica plays an important rôle. To attempt to interpret their behavior without taking this into account is to miss the meaning of some of the most important phenomena.

Dispersion in Water.

Silica is so abundant and so slightly affected by long contact with water that we easily forget it is most omnipresent in a highly dispersed condition. All natural waters contain silica. Silica constitutes, according to Clarke,[1] nearly 60 per cent of the lithosphere,[2] so that contact between water and silica is inevitable and dispersion into particles of colloidal size takes place in every spring or stream. High concentrations are not reached in this way, but from these dilute natural systems crystalline quartz and many silicious rocks have been laid down.

The first waters that condensed upon the surface of the earth must have flowed over igneous rocks and contained as one of their principal solid constituents, silica colloidally dispersed. Clarke[3] says that silicious deposits are formed by all waters containing silica but are commonly so small as to be inconspicuous. It may be here remarked that a thin gelatinous film of silica is always inconspicuous until dehydrated. Bastian,[4] speculating upon the origin of life, has been able to produce, under the influence of sunlight, cell-like structures from dilute solutions containing silica.[5] Under these conditions the silica tends to aggregate and yield structures so like living cells as to make this author believe that it was on this wise that life began on the earth.

Hydrous deposits of silica occur in nature as opal, and massive quan-

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[1] *Bull. U. S. Geol. Sur.*, 770, **20**, 26-34 (1924).
[2] Vail, James G., *J. Soc. Chem. Ind.*, **44**, 214T-219T (1925).
[3] Clarke, *loc. cit.*
[4] *Nature*, **92**, 579 (1914).
[5] Moore, Benjamin, and W. G. Evans, *Proc. Roy. Soc.*, ser. B, **89**, 17 (1915).

tities of silica gel were found in the course of excavating the Simplon Tunnel.[6]

Utilization of Silica by Certain Organisms.

Certain it is that many of the simpler forms of life use silica as an essential of their structure, building it into their framework in the most intricate and beautiful forms.   Such are the diatoms,[7] whose remains constitute vast deposits of nearly pure silica.   The great surface of diatomaceous earth makes it valuable for thermal insulation and other processes such as filtration where its structure distinguishes it from other forms of silica.   Higher organisms, among them the horse-tail rushes (equisetum) and certain cereal plants, notably rice, build large amounts of silica into their structures.   The former has enough to make it useful as an abrasive for cleaning metal ware.   The seed hulls of rice contain about 35 per cent of silica.[8]   Charred rice chaff after extracting with caustic soda is used to make absorbent carbon [9] and this process has been proposed as a source of commercial silicate of soda as a by-product.[10]   The ability of plants to disperse and coagulate silica has not been fully investigated.   Acheson showed that tannic acid or other vegetable extractive matter was useful for dispersion. Diatoms are able to disperse flocculent silicious precipitates.[11, 12]   The action of algae on volcanic waters,[13] running as in the case of the Opal Spring in Yellowstone National Park up to 700 parts per million, accounts for deposits of silicious sinter characteristic of various geyser beds.   Further evidence of this sort of action has been reported by Gesell [14] from experience in a paper mill.   He was able to produce a particularly tinny sheet of paper owing to the presence in the water of organisms which had the power of accumulating silica.

Baylis,[15] in his work dealing with the problems of municipal water works, also calls attention to the ability of algae to utilize silica from the water.   It seems fair to assume that the action of organisms which

[6] Spezia, G., *Atti accad. Sci. Torino,* **34,** 705 (1899).
[7] Richter, Oswald, *Aus Dem Pflanzen physiologischen Inst. der K.K. Deutschen Universität in Prag.,* No. **118,** 22 (1911).
[8] Blardone, George, U. S. Pat. 1,293,008 (Feb. 4, 1919).
[9] McKee, R. H., and P. M. Horton, *Chem. Met. Eng.,* **32,** 14 (1925).
[10] Puttaert, Jean François and Francis J. Puttaert, U. S. Pat. 1,588,335 (June 8, 1926).
[11] Acheson, Edward G., *Trans. Am. Ceram. Soc.,* **6,** 31-46 (1904).
[12] Richter, *loc. cit.*
[13] Weed, W. H., *Am. J. Sci.,* 3rd ser., **37,** 351 (1889).
[14] *Paper,* **33,** No. 23, 5-6 (1924).
[15] Baylis, John R., personal communication; *J. Am. Water Works Assoc.,* **9,** 712 (1922).

use silica has to do with accelerating or suppressing the tendency of the silica particles to become massed together and that this may take place in very dilute solutions. This power is especially remarkable in view of the difficulty of completely removing silica from dilute solution by precipitation or even repeated evaporation with acids, as in the ordinary course of analysis.

<center>BEHAVIOR OF SILICA SOLS.</center>

DEVELOPMENT OF COLLOIDAL PROPERTIES.

Silica freshly liberated by adding hydrochloric acid to a dilute solution of alkali metal silicate exists in a very fine state of dispersion. It will diffuse through an animal, collodion, or parchment paper membrane sufficiently fine in texture to retain colloidal silver.[16] It causes a depression of the freezing point of water [17] and an electrical conductivity which confirms the idea that the particle dimensions are more nearly like those of true solutions than like colloids. Mylius and Groschuff found a lowering in the freezing point of 0.118°. They observed only a slight decrease in the conductivity—0.4 per cent (14088-14032).

Egg albumen causes no precipitation at first, but changes soon take place. A silica sol which has aged, although it may remain liquid and appear superficially unchanged, will be retained by the membranes through which it previously passed; it no longer gives a measurable depression of the freezing point of water, and its conductivity has fallen practically to zero.[18, 19]

TENDENCY TOWARD GELATION.

If now the liquid sol be concentrated under reduced pressure, it becomes increasingly unstable and finally undergoes a rather sudden change in which the viscosity rises abruptly and the entire mass sets to a solid gel.[20] Silica gels containing three hundred molecules of water for each molecule of silica set to a firm texture, and any sol containing this amount of water or less tends to form a gel including the whole of the liquid.[21] The rate at which the changes take place depends upon concentration, purity, temperature, time, and degree of agitation. A

[16] Zsigmondy, Richard, and R. Heyer, *Z. anorg. Chem.*, **68**, 169-187 (1910).
[17] Mylius, F., and E. Groschuff, *Ber.*, **39**, 121, 124 (1906).
[18] Sabanejeff, *J. Russ. Phys. Chem. Soc.*, **21**, 515 (1889).
[19] Bruni and Pappada, *Gazz. Chim. Ital.*, **31** (1), 244 (1901).
[20] Graham, Thomas, *Phil. Trans.*, **151**, 205 (1861).
[21] Holmes, Harry N., "Colloid Symposium Monograph," Vol. **1** (1923), p. 25.

sol containing 1 per cent of silica may, under favorable circumstances, remain fluid for a year, but the higher concentrations are exceedingly unstable. It may be regarded as a rare accident if a pure sol containing 10 per cent of silica is obtained.[22] Such sols are so unstable that they gel very easily. Shaking of the containing vessel may be sufficient to cause the transition from liquid to solid. Graham,[23] whose classical studies laid the foundations of colloid chemistry, showed that the gels formed from silica sols developed with increasing speed, the greater the concentration.

Sols of substantially identical character can be prepared only by minute attention to the composition and concentration of silicate solutions, to strength of the acid and all the conditions of dialysis.[24]

Zsigmondy [25] was able to prepare sols of much greater purity than Graham and to follow their increasing instability by measuring osmotic pressure, which declined steadily with advancing age of the sol.

Ormandy [26] says that a silicic acid solution made by the electro-osmose process has, at the moment of its preparation, a molecular weight which corresponds to the formula H_2SiO_3 and that the molecular weight increases steadily with time until with a 10 per cent solution, after about six weeks, the molecular weight is of the order of 60,000 to 80,000 and separation takes place. The conductivity of such solutions, kept in paraffin wax-lined vessels, affords such a close index of the change that the age of the solutions can be estimated within a few hours.[27]

Electrolytes may precipitate or stabilize the sols and these tendencies affect the time of gelation of sols which contain electrolytes.[28, 29, 30]

If we assume that these phenomena are the result of a tendency on the part of very small particles of colloidal silica to gather together into clusters or masses until finally they become large enough and sufficiently immobile to produce first a viscous liquid and then a solid gel structure, we shall have a concept which, though it does not offer a complete explanation, at least fits in with a large number of observed facts and helps to correlate them.

[22] Zsigmondy, Richard, "Kolloidchemie," Leipzig: Otto Spamer, 1912, p. 145.
[23] Pro. Roy. Soc., 13, 336 (1864).
[24] Grundmann, W., Kolloid Z., 36, 328-331 (1925).
[25] Zsigmondy, R., "Kolloidchemie," p. 149.
[26] Ormandy, W. R., "The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions," Report of Joint Discussion of Faraday Society and the Physical Society of London, 1920 (Oct. 25), p. 143.
[27] Searle, A. B., "Third Colloid Report of the British Assoc. for the Advancement of Science," 1925, p. 123.
[28] Zsigmondy and Heyer, loc. cit.
[29] Werner, J. Am. Pharm. Assoc., 9, 501 (1920).
[30] Krôzer, Kolloid Z., 30, 18 (1922).

TRANSITION FROM SOL TO GEL.

Zsigmondy stated that silica sols always tend to aggregate and form gels, but limited it to sols that had been well purified and were not too dilute. It has been found, however, that a large number of reactions of soluble silicates encountered in industry may be at least partly explained on the assumption that colloidal silica tends always to form larger particles and finally to produce a gel structure.[31, 32, 33, 34, 35, 36]
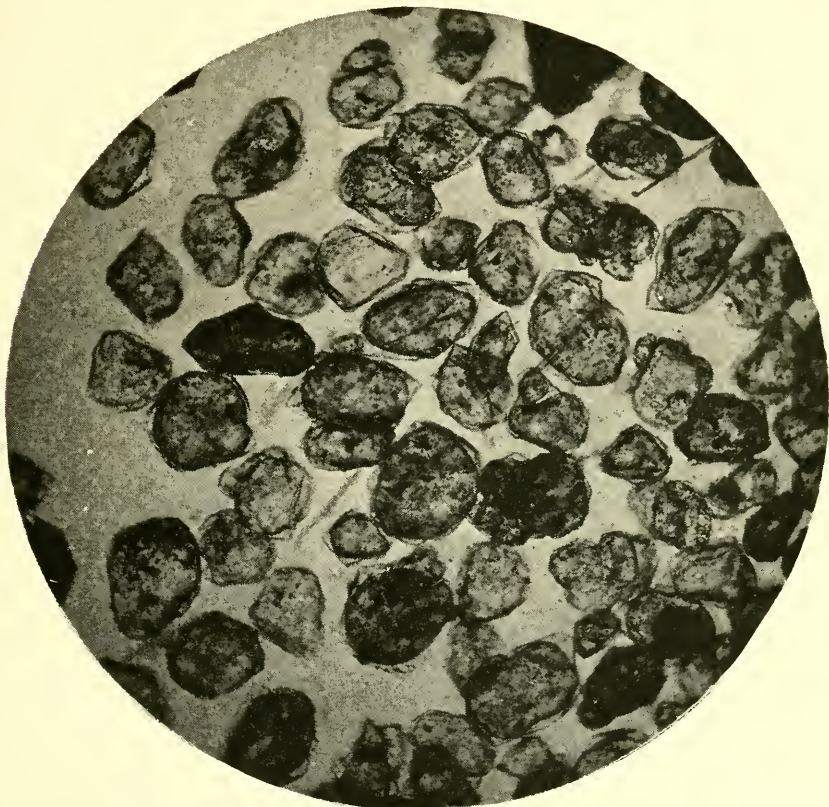
FIG. 1.—Growth of Silica Crystals on Rounded Grains of Sand.
(Courtesy C. L. Dake)

CRYSTALLIZATION.

Crystallization may take place from the same solutions which under other conditions form gels. Dake,[37] in his work on the St. Peter sandstone, has found small rounded sand grains upon which crystal faces

[31] Schwarz and Stowener, *Kolloidchem. Beihefte,* **19**, 171 (1924).
[32] Schwarz and Leide, *Ber.,* **53**, 1509, 1680 (1920).
[33] Schwarz and Leondard, *Kolloid Z.,* **28**, 77 (1921).
[34] Zsigmondy and Spear, "Chemistry of Colloids," **1917**, p. 137.
[35] Grundmann, *Kolloidchem. Beihefte,* **18**, 197 (1923).
[36] Bachman, *Z. anorg. Chem.,* **100**, 1 (1917).
[37] *School of Mines and Met., U. of Missouri, Tech. Ser. Bull.,* **6**, No. 1 (1921).

·have grown. The grains have evidently been worn round by long continued attrition with the formation of colloidal silica from which, under other conditions, definite crystals could be developed.[38] Quartz crystals are built up very slowly from dilute sols. This is what we should expect, for crystals are arrangements of particles of atomic dimensions and silica sols contain these in a free condition for a short time only. Further, though the method of X-ray interference does not give any evidence of crystal structure in fresh silica gels, it is found in gels which have aged.[39] The particles of the fresh gel structure are then capable of rearrangement, a fact which we know also from the phenomenon of syneresis, in which the gel contracts and squeezes out some of the liquid phase.

STRUCTURE OF SILICA GELS.

Natural gels are familiar as opal. The rhythmic bands of agate resembling closely the rings formed by silica gels, in the experiments of Liesegang,[40] point strongly to the genesis of agates as gels. The enduring character of these minerals suggests that when it has once been formed, the gel structure of silica is not easily dispersed.[41, 42, 43] Agate must have remained for long periods of geologic time under water, becoming progressively harder until the point has finally been reached at which no definite gel structure can be detected. The work of Zsigmondy,[44] Patrick,[45] and others, has established the structure of silica gels as a system of pores in a solid phase. The silica particles, which have coalesced until their size became sufficient to permit adjacent particles to touch and form one unified mass, will of necessity have comparatively great spaces between them filled with the liquid phase from which the particles separated. The dimensions of these pores can be established only by their behavior, for they are ultramicroscopic. The amount of surface which can be exposed when such sols are dried is almost incredible. As we shall later return to the subject of gels, it will suffice, for the moment, to recall their very high capacity to adsorb vapors from gases and various colloid materials from organic liquids, as for instance, sulfur compounds in mineral oils.

[38] Spezia, G. J., *Atti Accad. Torino*, **34**, 705 (1899) ; *J. Chem. Soc.*, **76**, 300 (1899) ; **78**, 595 (1900).
[39] Scherrer, P., *Nachr. Ges. Wiss. Göttingen*, **96**, 100 (1918).
[40] Liesegang, R. E., *Z. anorg. Chem.*, **48**, 364 (1906).
[41] Holmes, Harry N., *J. Am. Chem. Soc.*, **40**, 1187-95 (1906).
[42] Zsigmondy, *op. cit.*, p. 166.
[43] *Centr. Mineral. Geol.*, 593-597 (1910) ; 497-507 (1911).
[44] *Anorg. Chem.*, **71**, 356 (1911).
[45] Patrick, W. A., and John McGavack, *J. Am. Chem. Soc.*, **42**, 947 (1920).

CONSTITUTION OF SOLUTIONS OF SODIUM SILICATES.

ELECTRICAL EVIDENCE.

Charges on Silica Particles. The ability of silica to adsorb ions has an important bearing upon the behavior at concentrations above those contemplated by Zsigmondy in his statement of the tendency of the particles to coalesce because the adsorbed material may, and frequently does, influence the rate at which such coalescence takes place, or in some cases inhibits it entirely. The colloidal particles of silica are, in general, negatively charged.[46] The electrolysis of an alkaline silicate solution is accompanied by migration of the silica particles toward the anode, and this condition persists except in solutions which have been made strongly acid.[47] The negative charge is steadily reduced by adding HCl and may be reversed without precipitation. Gordon [48] has shown the hydrogen-ion concentration at which the charge is reversed and has pointed out that this may be due to a dissociation of silica which acts like an acid radical until the hydrogen-ion concentration is raised to a point where this phenomenon is suppressed.[49]

TABLE 1. *Effect of pH on the Electrical Charge on Silica Gel.*

pH Values	Charge on Gel	Rate of Travel of Water in Mm. per Sec.	E.m.f.
6.526	Negative	6.3	116
4.717	Negative	3.1	120
3.567	Negative	2.4	120
1.217	Positive	1.4	119

Electrometric Titration of Silicic Acid. Electrometric titration curves are characteristic of dibasic acids suggesting the formula H_2SiO_3 with salts $NaHSiO_3$ and Na_2SiO_3.[50] This acid has been studied by dialysis and taking into account the portion which does not diffuse it is probably a much stronger acid than has been realized.

Multi-Charged Colloidal Micelles. If the colloidal silica particles are negatively charged and they continually tend to coalesce into larger particles without a change in the charge, it is convenient to assume the existence of charged colloidal micelles which McBain postulated in order to explain abnormally high conductivity of soap solutions. Negatively charged colloidal silica particles would tend to adsorb upon their

[46] Zsigmondy, R., *op. cit.,* p. 147.
[47] Stericker, Wm., Doctor's Thesis, University of Pittsburgh, **1922**, p. 6.
[48] Lösenbeck, *Kolloidchem. Beihefte,* **16**, 27 (1922).
[49] Gordon, Neil S., "Colloid Symposium Monograph," **2**, 119-121 (1924).
[50] Harman, *J. Phys. Chem.,* **31**, 616-625 (1927).

surfaces positively charged ions which may be present in solution. We may think of the more silicious sodium silicate solutions as containing much of their sodium content attached in this way to colloidal silica particles.

Electrical Conductivity. The work of Kohlrausch [51] on the conductivity of silicate solutions was the first to show evidence of a constitution in which colloidal silica exists along with sodium silicates which may be characterized as chemical individuals. He studied solutions of sodium metasilicate, Na_2SiO_3, and systems with more silica up to $Na_2O, 3.4SiO_2$ and found that the former conducted the current better in very dilute solutions than an equivalent concentration of any of the numerous salts he investigated. With rising concentration the conductivity fell off rapidly and concentrated solutions were found to be among the worst conductors. The metasilicate used was a crystalline commercial product with nine molecules of water and dissolved to a clear solution without residue. Its conductivity at high dilutions was 30 to 40 per cent better than sodium chloride. At 0.75 mol per liter the two salts were nearly equal, and in concentrated solutions the metasilicate was not more than one-third as good.

TABLE 2. *Conductivity of Sodium Metasilicate.*

Mols Na_2SiO_3 per Liter	Conductivity of Solution Hg = 1		Temperature Coefficient	Conductivity of Water for Dilution
0.0001	0.1363	$\times 10^{-8}$	0.0273	0.011
0.0005	0.6853	"	0.0249	0.013
0.0010	1.359	"	0.0232	0.014
0.0045	5.74	"	....	0.011
0.0225	27.73	"	....	0.01
0.0450	53.11	"	0.0216	....
0.1004	108.3	"	....	....
0.2008	198.3	"	0.0225	....
1.	670.	"	....	....
1.2650	763.9	"	0.0244	....
2.5290	1028.	"	0.0273	....
3.7930	1031.	"	0.0316	....
4.5000	963.9	"	0.0347	....
6.4	655.	"	0.0465	....

Long boiling of a strong solution of the metasilicate with silica yielded a solution containing 3.4 mols SiO_2 per mol Na_2O. This was at all dilutions an inferior conductor as compared with equivalent sodium chloride, though at concentration 0.0001 mol Na per liter it was nearly as good. As much more silica was present, the mobility was less than in the metasilicate solution. The conductivity fell off precipitously

[51] *Z. phys. Chem.*, **12**, 773-791 (1893).

as the concentration rose, and at 0.01 mol per liter and above it was the worst conductor of all the salts investigated.

TABLE 3. *Conductivity of $Na_2O, 3.4SiO_2$.*

Mols $Na_2O, 3.4SiO_2$ per Liter	Conductivity of Solution (1) Hg = 1	Temperature Coefficient
0.000157	0.1527×10^{-8}	0.0297
0.000788	0.605 "	0.0302
0.00788	4.863 "	0.0263
0.0788	38.86 "	0.0258
0.788	203.7 "	0.0288
1.576	279.4 "	0.0310
3.152	289.2 "	0.0369
3.693	265.7 "	0.0406

The conductivity of both solutions reached a maximum before saturation; in the case of Na_2SiO_3, 1055×10^{-8} at 3.2 mols per liter concentration or 17 per cent; and the $Na_2O, 3.4SiO_2$, 300×10^{-8} at 2.5 mols
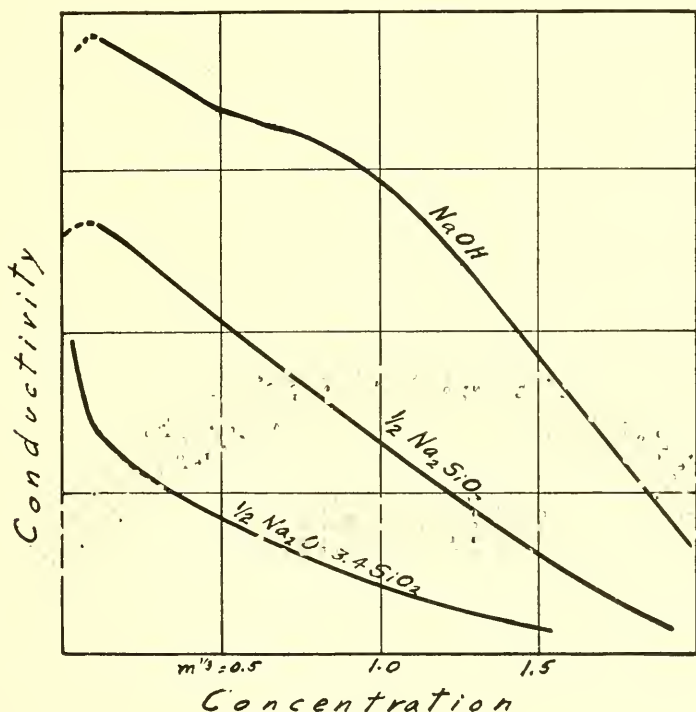

FIG. 2.—Conductivity and Concentration.

Na or 27 per cent. Kohlrausch also found an abnormal temperature coefficient of conductivity at all concentrations of the 1 : 3.4 ratio silicate. He expressed the opinion that this might be due to the breaking down of the silicate with increase of temperature. The metasilicate showed

no extraordinary change of conductivity with temperature except at extreme dilution.   Greater freedom of movement of the relatively large aggregates of silica at higher temperatures might also account for this.

In order to throw light on the condition of the excess of silica over that required to form Na_2SiO_3 in the more silicious silicates, mixtures were made in two series, the first beginning with NaOH and receiving $1:3.4$ silicate and the second beginning with $1:3.4$ silicate to which NaOH solutions were added. Conductivity was measured on these after
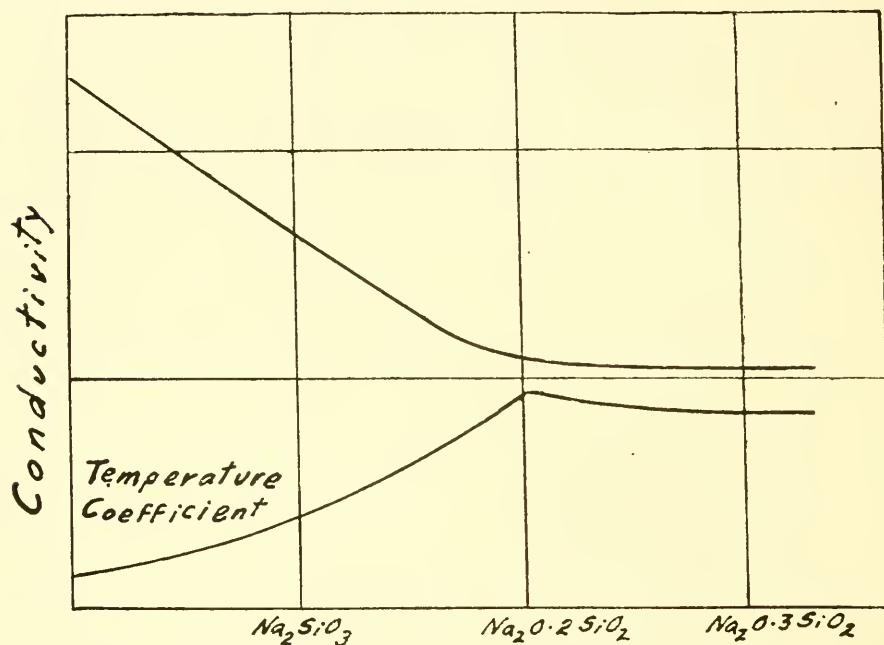
Fig. 3.—Effect of Increasing Silica on the Conductivity of Silicate Solutions.

they had come into equilibrium.   In the first series the conductivity decreased rapidly until the ratio $Na_2O, 2SiO_2$ was reached   Values for the higher ratios were only slightly smaller.   Conversely, the second series showed no real change until $Na_2O, 2SiO_2$ was reached, then the conductivity rose rapidly.   It is to be noted that there was no bend in either series corresponding to the ratio of Na_2SiO_3, the definite substance from which the study began.   The change of behavior corresponded to $Na_2Si_2O_5$ and the curve broke sharply at this point.   The temperature coefficient which increased from 0 to 2 did not change from 2 to the higher ratios.

Freshly diluted solutions showed higher conductivity than those which had stood.   The time required to reach equilibrium when mixtures of silicate with sodium hydroxide or of two silicates of different ratio were made, depended on the order of mixture and the composition

TABLE 4. *Conductivity with Changing Ratio.*

SiO₂ per Mol Na₂O	Conc. Na Mols per Liter	Conductivity	Temp. Coefficient
0	0.00955	1820×10^{-8}	. . . . .
0.209	0.00956	1685 "	. . . . .
0.419	0.00958	1330 "	. . . . .
0.632	0.00961	1420 "	. . . . .
0.829	0.00964	1290 "	. . . . .
1.035	0.00966	1156 "	. . . . .
1.237	0.00969	1031 "	. . . . .
1.44	0.00972	930 "	. . . . .
2.05	0.00980	667 "	. . . . .
2.53	0.00987	634 "	. . . . .
3.41	0.01000	614 "	0.0263
3.02	0.00994	627 "	. . . . .
2.53	0.00988	628 "	0.0265
2.04	0.00981	629 "	0.0274
1.54	0.00975	868 "	0.0243
1.00	0.00968	1183 "	0.0218
0.497	0.00961	1503 "	0.0204
0	0.00955	1826 "	0.0197

of the reacting solutions. Also the time which had transpired since the concentrated silicate solution was diluted had a marked influence. If the mixture contained less than two molecules of silica for each sodium (Na₂O) it came into equilibrium quickly. Its conductivity was the average of the conductivities of its components.

The following table shows the increase in conductivity readings above equilibrium after various time intervals from the mixing of 1 : 3.4 silicate which had stood three days since dilution to 0.01 mol Na per liter, with a sodium hydroxide solution to bring the ratio to 1 : 1.84.

TABLE 5. *Time Required to Obtain Equilibrium.*

Minutes	Conductivity Above Equilibrium	Minutes	Conductivity Above Equilibrium
0.	24.6	100.	6.9
0.5	24.5	120.	4.9
1.	24.2	160.	2.5
5.	22.9	180.	1.8
10.	21.8	200.	1.3
20.	20.0	250.	0.9
40.	16.4	300.	0.7
60.	12.9	500.	0.3
80.	9.7		

Potassium silicate with potassium hydroxide showed similar behavior, the initial conductivity being in some cases as much as 16 per cent above the equilibrium figure.

Kahlenberg and Lincoln [52] determined the conductivities of solutions made by adding sodium hydroxide solution to silica sols. They found

[52] *J. Phys. Chem.*, **2**, 77-90 (1898).

TABLE 6. *Conductivity of Silicate Solutions Prepared from Sodium Hydroxide and Silica Sol.*

Equivalent Conductivity at 25°C.

v	N	NaOH	Na$_2$SiO$_3$	NaHSiO$_3$	Na$_2$O, 5SiO$_2$
8	0.125	194.7	105.3	72.4	....
16	.0625	197.4	112.0	78.8	....
32	.03125	199.0	117.8	84.9	73.0
64	.01563	199.1	115.0	90.1	79.9
128	.00781	199.0	119.5	103.7	87.3
256	.00391	196.3	95.7 *	114.2	93.1
512	.00195	188.9	91.8 *	133.1	101.1
1024	.00098	181.8	104.8 *	148.5	113.3

v = volume in liters containing 1 gram molecule.
N = volume normality, i.e., gram molecules per liter of solution.

* Kahlenberg and Lincoln doubted these results because they were lower than those for NaHSiO$_3$.

that the freezing points of solutions of sodium metasilicate made in this manner did not differ greatly from those made from the metasilicate prepared by fusion and concluded from this that solutions made in the two ways were identical. From later work it seems highly improbable that this conclusion can be applied to solutions containing two or more equivalents of silica to one of sodium oxide and even the metasilicate solutions would probably show slight but distinct differences, as they did in freezing point determinations. The results obtained by Kahlenberg and Lincoln are given in Table 6. Hantzsch [53] also made some determinations, but they do not agree with any other results and are probably incorrect.

TABLE 7. *Equivalent Conductivity.*

T = 25°C.
Ratio Na$_2$O : SiO$_2$

N$_w$	NaOH	2:1	1:1	1:1*	1:1.5	1:2	1:3	1:4
2.0	142.0	57.32	57.25	57.50	32.09	25.80	20.46	16.17
1.0	172.5	85.57	81.25	81.20	50.23	36.10	31.42	23.24
0.5	200.0	107.80	96.80	96.5	66.75	49.05	45.41	33.14
0.2	209.0	136.90	112.70	113.0	86.20	62.59	57.33	48.25
0.1	214.5	157.5	130.80	130.0	99.20	72.70	66.48	57.80
0.05	220.0	175.5	143.8	142.6	107.04	78.00	75.63	65.80
0.02	225.5	190.1	152.7	151.8	114.20	84.00	81.75	75.06
0.01	227.5	193.0	155.0	156.0	118.10	89.50	85.16	81.50
0.005	228.0	194.2	158.0	159.0	120.14	93.20	89.90	86.04
0.0	....	....	160.0	....	121.00	95.00	91.00	88.00

* Figures taken from Kohlrausch.

$$\text{Equivalent conductivity} = \frac{\lambda (1000 + X)}{N_w P}.$$

Where λ = specific conductivity.
X = no. grams solid in 1000 gms. water.
N$_w$ = weight normality, i.e., gram molecules of solute per 1000 gms. of water.
P = density of the solution.

[53] *Z. anorg. Chem.*, **30**, 289-324 (1902).

Harman [54] confirmed and extended the work on conductivity and calculated equivalent conductivities.

Plotting these against concentration, he points out the following:

"(1) Ratio 1 : 1, i.e., sodium metasilicate, Na_2SiO_3, has a very high conductivity in dilute solution.

"(2) Ratio 2 : 1 gives practically the same values as 1 : 1 at concentrations 1–2 N_w. This is very remarkable.
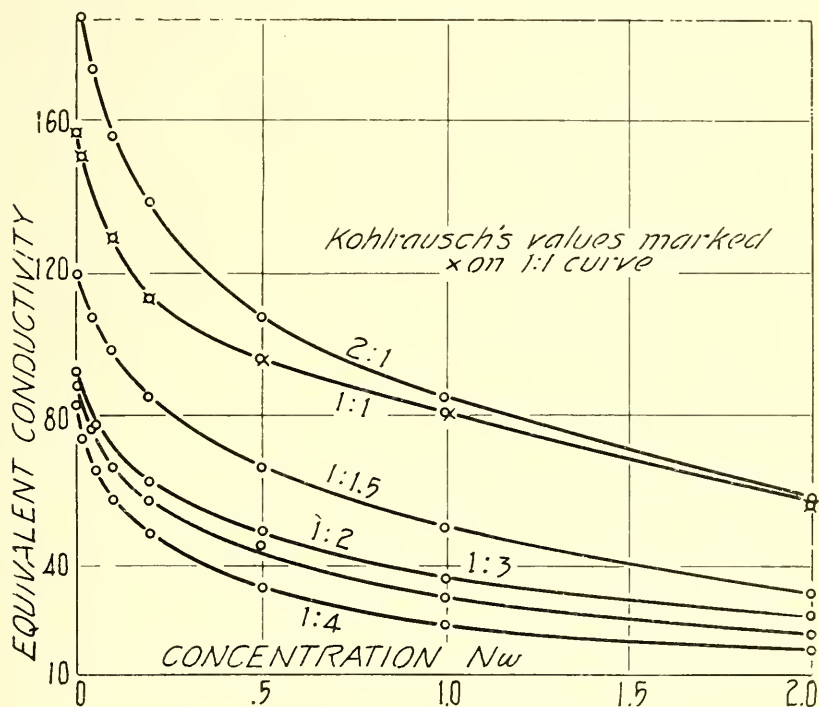

Fig. 4.—Equivalent Conductivity.

"(3) All the other ratios are quite fair conductors in dilute solution, but show an abnormally low conductivity in concentrated solution, especially the higher ratios 1 : 3 and 1 : 4."

Plotting equivalent conductivity against ratio, a sharp break in the curves seems to indicate the presence of $Na_2O \cdot 2SiO_2$ in solution and similar deviations suggest but do not prove that $2Na_2O \cdot SiO_2$ and Na_2SiO_3 are also present in the more concentrated solutions.

Kohlrausch and the other earlier investigators had concluded that the high conductivity in dilute solutions was due to hydrolysis. This seemed a reasonable basis on which to explain the abnormally high values for dilute solutions of metasilicate. In these solutions the salt

was supposed to be almost completely converted into sodium hydroxide and "silicic acid".

Later work, especially after methods of measuring the hydroxyl ion concentration had been developed, indicated the hydrolysis was not so great as had been assumed. Harman [55] found that when this hypothesis was tested on a quantitative basis, it was inadequate. "Hydrolysis into NaOH and colloidal silicic acid cannot account for this high conduc-
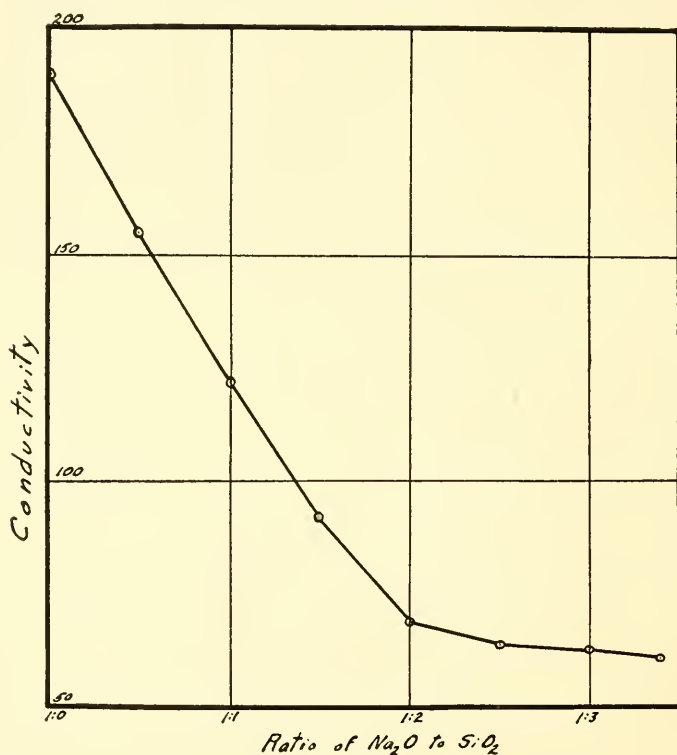

Fig. 5.—Variation of Conductivity with Ratio.

tivity, not even with ratios relatively rich in NaOH, nor in dilute solution where hydrolysis is greatest, and with ratios rich in silica, where hydrolysis is practically negligible, it is apparent that the explanation that the conductivity is due to hydrolysis is totally inadequate."

This does not mean that hydrolysis is not a factor nor that the hydroxyl ions formed do not carry a portion of the current in solutions containing less than two equivalents of Na_2O. But, "In ratios 1 : 2, 1 : 3, and 1 : 4 where the hydroxyl-ion concentration is very low, even in dilute solution, the fair conductivity of dilute solutions points to a high degree of ionization and a fairly mobile silicate ion, while in concentrated

[55] *J. Phys. Chem.*, **32**, 44 (1928). Summary article.

solution there may be either very little ionization or there may be complex or colloid formation." [56]

Kohlrausch pointed out that if the conductivity of the metasilicate were to be explained by dissociation into 2Na and SiO_3 ions, it would necessitate the assumption that the mobility of the latter exceeds that of the Cl ion by 70 per cent, which seemed improbable. If, however, we assume partial hydrolysis of the metasilicate, the mobility of the silicate ion would not be as high. Harman calculated from measurements of the freezing points and concentrations of sodium and hydroxyl ions the mobility of the silicate ions. Assigning values of 45 and 180 to the sodium and hydroxyl ions respectively he obtained these results:

TABLE 8.

Ratio $Na_2O : SiO_2$	Mobility of Silicate Ion in Dilute Solution
1 : 1	60
1 : 2	35
1 : 3	43
1 : 4	41

The idea of a multi-charged micelle put forward by McBain [57] in connection with soap solutions might offer a more satisfactory explanation. He had pointed out that sodium silicate solutions are also "colloidal electrolytes". This theory would explain the observed changes. Thus, when the silicate solution was highly dilute, the many charges upon the colloidal aggregates would make for high conductivity. As concentration increased the coalescence of the multi-charged micelles would proceed and their mobility would decrease.

Transport Numbers. Harman undertook some transport number experiments which he hoped "would produce some evidence as to whether the silica existed as colloid, simple ions, aggregates of simple ions carrying a sum total of their separate charges (i.e., ionic micelles), or as complex ions". [58] He obtained the following values by analyses of the liquids in anode, cathode, and intermediate chambers.

"Considering first the ratio 1:1, i.e., sodium metasilicate, it is seen that the mean of the six values of n_{Na} is 0.31, of n_{SiO_3}, 0.16, and n_{OH} 0.53. The proportion of the current carried by the silicate ions is very small, being only about one-half that carried by the sodium ions, while over one-half the total current is carried by the hydroxyl ions. This latter result was to be expected, since e.m.f. measurements show

[56] Harman, *J. Phys. Chem.*, **29**, 1162-3 (1925).
[57] McBain and Salmon, *J. Am. Chem. Soc.*, **42**, 426-60 (1920).
[58] *J. Phys. Chem.*, **30**, 359-368 (1926).

TABLE 9. *Transport Numbers.*

No. of Expt.	Ratio	Approx. N_w	n_{Na}	n_{SiO_3}*	By Difference $n_{OH} = 1$ $-(n_{Na} + n_{SiO_3})$
1	1 : 1	2.36	0.27	0.17	.56
2	1 : 1	1.0	.36	.13	.51
3	1 : 1	0.10	.31	.18	.51
		Mean	.31	.16	.53
4	1 : 2	1.0	.42	.88	...
5	1 : 2	0.5	.35	.70	...
6	1 : 2	0.1	.45	.87	...
		Mean	.41	.82	...
7	1 : 3	1.0	.40	1.35	...
8	1 : 3	0.5	.45	1.42	...
		Mean	.43	1.38	...
9	1 : 4	1.0	.53	2.32	...
10	1 : 4	0.1	.44	2.44	...
		Mean	.48	2.38	...

*These values as calculated disregard the possibility of the existence of $HSiO_3$ ions or of more complex ions containing more than one mol of SiO_2, e.g. $SiO_3.2SiO_2$.

that 10 to 30 per cent of the silicate is hydrolyzed according to the concentration, and the hydroxyl ion moves four times as fast as the sodium ion. In caustic soda n_{Na} is 0.2, and n_{OH} is 0.8; therefore the present result, where n_{OH} is not even double n_{Na}, shows that the concentration of the hydroxyl ions is not nearly equivalent to that of the sodium ions.

"The T.N. of sodium metasilicate shows no evidence whatever of any complex silicate ions or of micelle formation. If the silica is colloidal with OH ions adsorbed, such a high mobility as 70 would not be expected, as hitherto measurements have shown that such colloidal particles have a mobility approaching that of the slowest moving ions.

"When we look at the results obtained with ratio 1:2, 1:3, and 1:4, we at once notice the very high transport numbers of the silicate anions. They are for ratios 1:3 and 1:4, much greater than unity. The average value for ratio 1:2 is 0.88, for ratio 1:3, 1.44, and for ratio 1:4, 2.38, while the T.N. of the sodium remains much the same, about 0.45 in each case.

"Further, the T.N. for the silicate ion is approximately twice that of the sodium ion in ratio 1:2, three times in ratio 1:3, and four times in ratio 1:4. This high T.N. for the silicate ion at once points to the fact that the anion cannot possibly be the simple ion SiO_3^{--}, nor in fact should we expect it to be."

He concludes that:

"Ratio 1:1 evidently ionizes to Na^+, OH^- and SiO_3^{--} ions; n_{SiO_3} is small, n_{OH}, found by difference, is large.

"In ratios 1 : 2, 1 : 3, and 1 : 4, the T.N. of the silicate ion is high, and the silicate anion contains more than $1(SiO_2)$ per divalent charge; the average number of mols SiO_2 per divalent charge being equal to the ratio.

"The mobility of the SiO_3 ion in ratio 1 : 1 is about 70. In ratios 1 : 2, 1 : 3, and 1 : 4, it is approximately equal to that of the sodium ion, thus agreeing with mobilities calculated from conductivity experiments.

"In ratios 1 : 2, 1 : 3, and 1 : 4, the silicate anion is not the simple SiO_3^{--} ion, but is either an aggregation of simple silicate ions with or without colloidal silica, or a definite complex silicate ion."

Although the constitution of the anions is still an open question, this work proved that the silicate ions in the ratios of 1 : 2 and above did carry the current, in spite of the earlier investigators' assumption that they could not.

Hydrogen-Ion Concentration. Therefore, the discrepancy which was apparently raised by Bogue's electrometric determinations of the hydrogen-ion concentration has been explained. Bogue [59] worked with sodium metasilicate and a series of commercial silicate of soda solutions of higher silica ratio up to approximately $Na_2O, 4SiO_2$. His results are given in Table 10.

TABLE 10. *Values Obtained for Each Silicate at Various Dilutions.*

Silicate No. 1. $Na_2O, 3.97SiO_2$

Volume Con- taining 1 Gr. Molecule	pH	OH × 10⁻⁴	Hydrolysis *Per Cent*
3.3	11.01	10.2	0.20
10	10.80	6.4	0.38
20	10.77	6.0	0.68
50	10.61	4.13	1.11
100	10.48	3.00	1.58

Silicate No. 2. $Na_2O, 3.48SiO_2$

3.3	11.08	12.1	0.24
10	10.90	8.2	0.49
20	10.82	6.6	0.75
50	10.67	4.76	1.28
100	10.52	3.36	1.77

Silicate No. 3. $Na_2O, 2.93SiO_2$

3.3	11.23	17.6	0.35
10	11.08	12.0	0.71
20	10.92	8.4	0.95
50	10.77	5.95	1.60
100	10.57	3.72	1.96

[59] Bogue, R. H., *J. Am. Chem. Soc.*, 32, 2575-2582 (1920).

TABLE 10. *Values Obtained for Each Silicate at Various Dilutions—(Continued).*

Silicate No. 4. $Na_2O, 2.48SiO_2$

Volume Con- taining 1 Gr. Molecule	pH	OH × 10⁻⁴	Hydrolysis *Per Cent*
3.3	11.36	23.4	0.46
10	11.16	14.5	0.85
20	11.02	10.8	1.23
50	10.84	6.95	1.87
100	10.69	4.94	2.60

Silicate No. 5. $Na_2O, 2.11SiO_2$

3.3	11.74	54.8	1.08
10	11.50	32.0	1.88
20	11.25	18.0	2.04
50	10.93	8.8	2.37
100	10.77	6.0	3.15

Silicate No. 6. $Na_2O, 1.63SiO_2$

3.3	12.18	155.0	3.05
10	11.95	90.0	5.29
20	11.63	53.5	6.08
50	11.42	26.8	7.21
100	11.24	17.6	9.27

Silicate No. 7. $Na_2O, 1.11SiO_2$

3.3	12.69	504.0	9.92
10	12.43	275.0	16.18
20	12.21	162.0	18.40
50	11.93	85.0	22.81
100	11.73	54.0	28.43

Three assumptions were made, namely, (1) that if no hydrolytic dissociation had occurred, the hydroxyl-ion concentration would be the same as that of water at the same temperature, (2) that if hydrolytic dissociation had proceeded to completion, the hydroxyl-ion concentration would be the same as that of an equivalent solution of sodium hydroxide, (3) that the hydroxyl-ion concentration is a straight-line function of the degree of hydrolysis.

Although his work confirmed the findings of the earlier investigators that the hydrolysis is most nearly complete in the metasilicate and that the degree of hydrolysis is less as the relative amount of silica is increased, the amount of hydroxide formed was very much less than had been thought previously. At a dilution of 100 liters per gram molecule the metasilicate was only 28.43 per cent hydrolyzed, less than a third as much as had been assumed. The degree of hydrolysis in the more silicious solutions at this concentration varied from 9.27 to 1.58 per cent.

Stericker [60] recalculated Bogue's results to show the amounts of

[60] *Chem. & Met. Eng.*, **25**, 61 (1921).

silicate of each type in contrast with the amount of sodium hydroxide present in each 100 cc. of solution, as follows:

TABLE 11. *Concentration of Sodium Hydroxide in Sodium Silicate Solutions at 30°C.*

	$Na_2O, 1.11SiO_2$		$Na_2O, 1.63SiO_2$		$Na_2O, 2.11SiO_2$	
	Silicate	NaOH	Silicate	NaOH	Silicate	NaOH
0.33 molar	3.70	0.1205	4.605	0.0364	5.51	0.0239
0.10 molar	1.22	0.0647	1.52	0.0212	1.82	0.0082
0.05 molar	0.61	0.0369	0.76	0.0122	0.91	0.0041
0.01 molar	0.122	0.0115	0.152	0.0038	0.182	0.0013

	$Na_2O, 2.48SiO_2$		$Na_2O, 2.93SiO_2$	
	Silicate	NaOH	Silicate	NaOH
0.33 molar	6.42	0.0056	7.34	0.0042
0.10 molar	2.12	0.0034	2.42	0.0029
0.05 molar	1.06	0.0024	1.21	0.0019
0.01 molar	0.212	0.0011	0.242	0.0008

	$Na_2O, 3.48SiO_2$		$Na_2O, 3.97SiO_2$	
	Silicate	NaOH	Silicate	NaOH
0.33 molar	8.245	0.0029	9.15	0.0024
0.10 molar	2.72	0.0020	3.02	0.0015
0.05 molar	1.36	0.0015	1.51	0.0014
0.01 molar	0.272	0.0007	0.302	0.0007

Silicate = grams of silicate of the given formula per 100 cc. of solution.
NaOH = grams of NaOH per 100 cc. of solution.
It will be noted that these figures are approximate percentages.

Thompson [61] conducted studies at higher concentrations than Bogue. He set out to find by physical measurements differences between highly concentrated sodium silicate solutions which, though of substantially the same chemical composition, behaved differently in industrial processes. He measured hydrogen-ion concentrations and freezing point depressions,* and developed a theory of the constitution of sodium silicate solutions. Six samples formed the basis of his work.

TABLE 12. *Analysis of Commercial "Alkaline" Silicates.*

	A	B	C	D	E	F
SiO_2	29.01	....	35.6	34.78	37.44	1.725
Na_2O	8.94	....	16.55	17.83	17.08	....
R_2O_3	....	....	.67	.20	.15	....
CO_2	....	....	....	.94	1.21	....
SO_3	....	....	.12	.54	.39	....
Cl	....	....	.19	.20	.22	....
H_2O	61.56	....	46.8	45.62	43.35	....
Sp. gr.	1.415	1.690	1.707	1.707	1.700	1.725

All of these, with the exception of A, closely approximated the composition $Na_2O, 2SiO_2$. Table 13 shows the pH values which he

[61] Thompson, Lincoln, Master's Thesis, Worcerter Polytech. Inst. 1923.
* Cf. pages 40-44, 61-63.

found. It should be noted that a normality of 1.632 corresponds to 21.5 grams solids in 100 cc. of solution in the case of the 1:3.3 ratio silicate. Likewise, the normality of 3.65 for the 1:2 ratio means 34.6 grams solids in 100 cc. of solution. Thompson found higher pH values in three freshly diluted solutions than in the same after standing. The effect of freezing the silicates solidly for an hour was also studied but was not found to influence the pH value after standing a few hours.

When Thompson plotted Bogue's values with the pH figures as ordinates and the Na_2O,SiO_2 ratios as abscissae, he found, as Kohlrausch had for conductivity, a sharp break in the curve at $Na_2O, 2SiO_2$. From this he postulated that sodium silicate solutions of less sodium content than is indicated by the ratio $Na_2O, 2SiO_3$ are composed of $Na_2Si_2O_5$ and free silicic acid while those of more sodium than the ratio indicates contain free sodium hydroxide and sodium disilicate. It is not unlikely that either sodium metasilicate or sodium disilicate may be present in concentrated silicate solutions. But the hydroxyl-ion concentrations prove that the relation is not as simple as that suggested by Thompson.

TABLE 13. *Thompson's Hydrogen Electrode Measurements.*

Silicate A $Na_2O, 3.3SiO_2$ Volume Normality	pH	Silicate E $Na_2O, 2.25SiO_2$ Volume Normality	pH	Silicate C $Na_2O, 2.21SiO_2$ Volume Normality	pH	Silicate D $Na_2O, 2.01SiO_2$ Volume Normality	pH
1.632	11.42	3.378	12.18	3,286	12.16	3.652	12.49
.816	11.36	3.116	12.13	2.592	12.09	2.781	12.37
.680	11.20	1.689	12.08	1.325	12.07	2.739	12.35
.204	10.70	1.631	12.03	1.296	12.00	2.642	12.33
.157	10.59	.845	11.96	.8258	11.91	2.191	12.28
.119	10.53	.769	11.90	.6628	11.83	1.684	12.26
.107	10.50	.576	11.83	.648	11.81	1.321	12.20
.0669	10.48	.432	11.70	.5456	11.80	.9169	12.11
.0487	10.38	.216	11.57	.334	11.76	.8419	12.06
.0297	10.23	.0576	11.05	.2498	11.54	.6604	11.96
.0201	10.05	.0288	10.73	.167	11.49	.2292	11.76
.0101	9.80	.0144	10.40	.136	11.35	.05733	11.10
				.0627	11.04		
				.03404	10.95		

Silicate B Approx. $Na_2O, 2SiO_2$ Volume Normality	pH	Silicate F Approx. $Na_2O, 2SiO_2$ Volume Normality	pH
3.2	12.40	3.1	12.03
1.6	12.23	1.55	11.90
.8	12.10	.78	11.70

Harman [62] extended this investigation of hydroxyl-ion concentrations and calculated hydrolysis as shown in the following table:

[62] *J. Phys. Chem.,* 30, 1100-1111 (1926).

TABLE 14. *Electrometric Measurements of Hydrolysis.*

N_w	E.m.f. corrected	pH	(H·)	(OH')	Per Cent Hydrolysis Calc. from NaOH Which Gives Expt. (OH)	Per Cent Hydrolysis Calc. from Exptly. Found (OH) Ion Alone
			Ratio 2:1.			
2.0	1.483	13.48	0.33×10^{-13}	0.29	17.5	14.5
1.0	1.0334	13.23	0.59	0.165	19.0	16.5
0.398	1.059	12.93	0.12×10^{-12}	0.0804	22.6	20.2
0.159	0.9981	12.63	0.235	0.0424	28.3	26.6
0.0398	0.9697	12.12	0.77	0.01297	32.6	32.6
0.0159	0.9455	11.74	0.18×10^{-11}	0.0056	36.0	35.0
			Ratio 1:1.			
2.435	1.0490	13.49	0.325×10^{-13}	0.295	14.8	12.1
1.133	1.0328	13.22	0.600	0.163	16.3	14.3
0.547	1.0181	12.97	0.11×10^{-12}	0.0896	18.7	16.3
0.204	0.9956	12.59	0.255	0.0388	20.0	19.0
0.1	0.9798	12.32	0.48	0.0207	21.8	20.7
0.05	0.9628	12.04	0.91	0.011	22.6	22.0
0.02	0.9406	11.67	0.215×10^{-11}	0.00465	23.25	23.25
0.01	0.9274	11.44	0.36	0.00278	27.8	27.8
			Ratio 1:1.5.			
2.0	1.0046	12.74	0.18×10^{-12}	0.054	3.0	2.7
1.0	1.0040	12.73	0.185	0.0532	5.9	5.3
0.5	0.9915	12.52	0.30	0.0329	7.0	6.6
0.2	0.9724	12.20	0.63	0.0158	8.25	7.9
0.1	0.9574	11.95	0.115×10^{-11}	0.00868	8.7	8.9
0.05	0.9424	11.69	0.205	0.00488	9.7	7.7
0.02	0.9218	11.34	0.46	0.0022	11.0	11.0
0.01	0.9064	11.08	0.83	0.0012	12.0	12.0
			Ratio 1:2.			
2.450	0.9720	12.19	0.645×10^{-12}	0.0152	0.65	0.62
1.110	0.9677	12.12	0.76	0.013	0.21	1.01
1.0	0.9678	12.12	0.76	0.013	1.35	1.3
0.5	0.9584	11.96	0.11×10^{-11}	0.0091	1.88	1.8
0.204	0.9424	11.69	0.205	0.00486	2.38	2.4
0.1	0.9290	11.46	0.35	0.00285	2.85	2.8
0.05	0.9180	11.28	0.53	0.0019	3.8	3.8
0.021	0.9034	11.03	0.935	0.00107	5.1	5.1
0.011	0.8924	10.84	0.14×10^{-10}	0.000714	6.5	6.5
			Ratio 1:3.			
2.0	0.9196	11.31	0.49×10^{-11}	0.00202	0.101	0.101
1.0	0.9190	11.29	0.515	0.00192	0.192	0.192
0.5	0.9170	11.27	0.55	0.00180	0.36	0.36
0.2	0.9060	11.07	0.85	0.00117	0.57	0.57
0.1	0.8954	10.89	0.13×10^{-10}	0.00768	0.77	0.77
0.05	0.8854	10.73	0.185	0.00054	1.10	1.10
0.02	0.8651	10.38	0.42	0.00024	1.20	1.20
0.01	0.8324	9.83	0.14×10^{-9}	0.000069	1.38	1.38

TABLE 14. *Electrometric Measurements of Hydrolysis—(Continued).*

N_w	E.m.f. corrected	pH	(H·)	(OH')	Per Cent Hydrolysis Calc. from NaOH Which Gives Expt. (OH)	Per Cent Hydrolysis Calc. from Exptly. Found (OH) Ion Alone
			Ratio 1 : 4.			
2.0	0.8904	10.81	0.155×10^{-10}	0.000638	0.032	0.032
1.0	0.8934	10.86	0.14	0.000709	0.071	0.071
0.5	0.8916	10.84	0.14	0.000711	0.14	0.14
0.2	0.8921	10.84	0.14	0.000712	0.35	0.35
0.1	0.8869	10.75	0.175	0.00057	0.57	0.57
0.05	0.8818	10.67	0.215	0.000464	0.93	0.93
0.02	0.8675	10.42	0.38	0.00026	1.30	1.30
0.01	0.8534	10.18	0.66	0.00015	1.50	1.50

These figures are not directly comparable with those obtained by Bogue and Thompson because they are based on weight normality while the others are on the basis of volume. In addition, Harman made a correction for the liquid potential difference which Bogue did not apply. In spite of these differences, the results, shown graphically below, are in general agreement with those of Bogue.
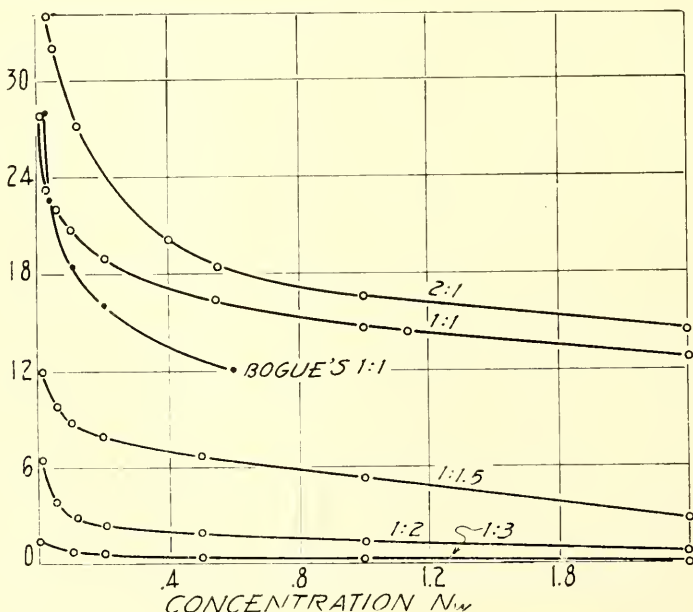
FIG. 6.—Percentage Hydrolysis against Concentration.

Therefore Harman concluded that :

"None of these silicates are largely hydrolyzed. At 0.01 N_w, Na_2SiO_3 is only 27.8 per cent hydrolyzed, while ratios 1 : 3 and 1 : 4 at the same concentration show only 1.5 per cent hydrolysis.

"In concentrated solution the percentage hydrolysis is very low.

"It appears probable that much of the silica is present as simple and complex silicate ions (and ionic micelles). This also accounts for the good conductivity and the high transport numbers."

These results further emphasize the misleading character of some of the methods which have been proposed for the determination of free
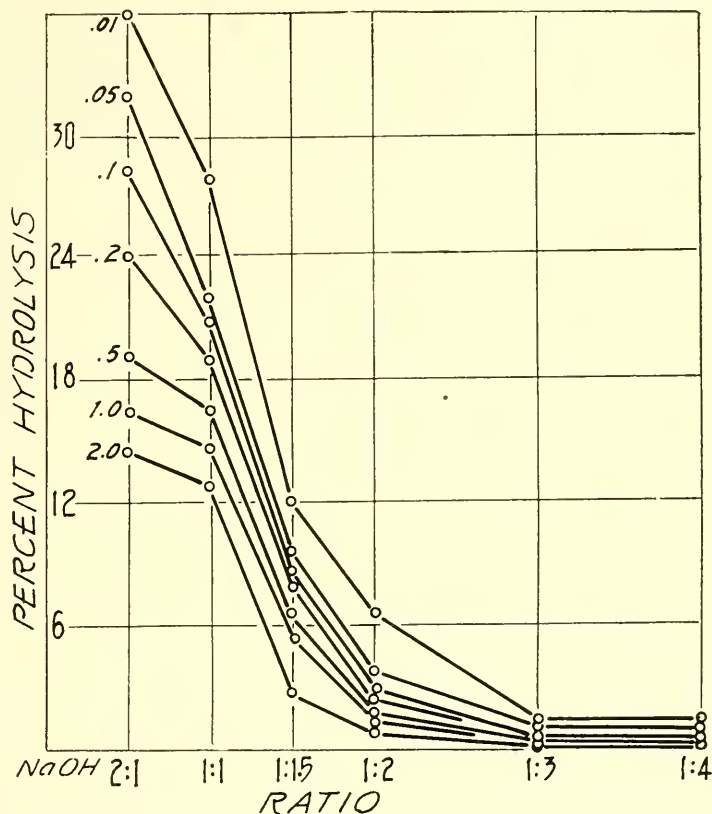
Fig. 7.—Percentage Hydrolysis against Ratio.

alkali in commercial silicate solutions. The assumption that some definite compound such as $Na_2Si_4O_9$ is waterglass, and that alkali found by analysis in excess of that required to satisfy this or some other arbitrarily chosen formula, is present as sodium hydroxide is particularly misleading.

Special Effects in Concentrated Solutions. It must also be remembered that even if dilute solutions are highly hydrolyzed, it does not follow that the same is true of concentrated solutions. The work thus far cited shows plainly that the hydrolysis is less as the concentration rises. Equilibrium is attained slowly in concentrated solutions and rearrangements result from such simple processes as dilution or

changing the temperature. A flocculent precipitate has been observed to form at the interface when water is poured over a concentrated viscous solution of $Na_2O, 2SiO_2$. Attempts to titrate concentrated solutions result in the separation of gels and their behavior toward indicators which may be adsorbed on the colloid particles further complicates studies directed to throw light on their constitution.

EFFECTS DUE TO NUMBER OF PARTICLES.

Freezing Points. Bogue pointed out the possibility that colloidal silica might be able to adsorb hydroxyl ions or otherwise interfere with their effect. Thus the electrometric method for determining hydrogen-ion concentration shows the actual alkalinity of one phase rather than of the whole system. If this were the case the hydroxyl ion adsorption would have to be great, especially with higher silica ratios. Therefore, the osmotic activity would be very small. On the other hand, if the activity is large, it will indicate the concentrations found by means of the hydrogen electrode are correct.

The first work of interest in this connection is that of Kahlenberg and Lincoln.[63] Their observations covered the silicates of sodium, potassium, lithium, rubidium, and caesium, and included measurements of freezing point depressions at high dilutions.

TABLE 15. *Freezing Point Depression.*

V	Freezing Pt. Depression	Calc. Mol. Wt.	Mol. Wt. NaOH	Prep'd by Fusion	Calc. Mol. Wt.
8	0.695	41.3	27	...	...
12	0.498	38.4	26.2	...	...
16	0.385	37.3	24.4	...	...
24	0.280	34.2	23.9	...	...
32	0.210	34.9	22.4	0.200	36.5
48	0.150	31.9	20.9	0.140	34.8
64	0.110	32.6	21.4	0.108	33.8
96	....	...	...	0.077	31.6

V = concentration expressed as liters containing 1 mol of solid Na_2SiO_3, mol. wt. 121.58.

Their method of preparation was to mix sols of silicic acid prepared by dialysis, according to Graham,[64] with hydroxides of the alkali metals. They showed that in the case of sodium metasilicate this procedure yielded a solution with a freezing point depression not greatly but appreciably different from the metasilicate produced by fusing silica

[63] Kahlenberg and Lincoln, *J. Phys. Chem.*, **2**, 77-90 (1898).
[64] Graham, *Phil. Trans.*, **151**, 205 (1861).

with the alkaline carbonate. The differences would probably be much greater with the more silicious silicates, which Kohlrausch showed reached a condition of equilibrium very slowly. Comparison of these solutions by the conductivity method showed them alike but still leaves a question about the more concentrated and more silicious silicate solutions.

Kahlenberg and Lincoln studied also the ratios $Na_2O, 2SiO_2$ and $Na_2O, 5SiO_2$. Expressing the former as $NaHSiO_3$, mol. wt. 100.1, they found the following:

TABLE 16. *Freezing Point Depression.*

V	Observed Freezing Point Lowering	Calc'd. Mol. Wt.	NaOH Mol. Wt.
8	0.332	70.9	31.
12	0.263	59.7	26.1
16	0.202	58.3	25.5
24	0.146	53.7	23.5
32	0.110	53.5	23.4

And for $Na_2Si_5O_{11}$ = mol. wt. 361.34

32	0.178	119.9	27.
48	0.139	102.4	23.1
64	0.104	100.3	22.6
96	0.089	79.9	18.
128	0.059	90.4	20.4

V = volume in liters in which one gram-molecule of the salt expressed by the formula is contained. Third column—molecular weights calculated on the supposition that the salt when in solution has the composition indicated by the formula.

These figures do indicate high osmotic activities, which Kahlenberg and Lincoln attributed to the formation of sodium hydroxide by the hydrolysis of the silicates. This explanation agreed with the facts that were then known (1898), but not with those found by the hydrogen electrode and transport number experiments.* Another explanation would be that silicate ions are formed, which would be in accord with all the facts so far presented.

Thompson determined freezing points of three of the silicates with which he worked.† The lowering of freezing points is summarized in the curve.

The freezing point lowering was somewhat greater for a freshly diluted solution than for one that had reached equilibrium, which was accomplished after a few hours but not fully studied.

* Cf. pages 31-39.
† Cf. pages 42, 44.

TABLE 17. *Thompson's Freezing Point Results.*

Silicate D Na₂O, 2.01SiO₂		Silicate C Na₂O, 2.21SiO₂		Silicate E Na₂O, 2.25SiO₂	
Normality	Freezing Point Lowering	Normality	Freezing Point Lowering	Normality	Freezing Point Lowering
3.37	3.31	2.652	2.59	3.227	2.93
2.781	2.74	2.592	2.59	3.08	2.82
2.642	2.67	1.39	1.56	1.614	1.63
1.684	1.80	1.325	1.52	1.54	1.63
1.668	1.79	1.296	1.56	1.076	1.245
0.842	1.15	0.60	1.00	0.807	1.07
0.695	1.03	0.6628	1.03	0.779	1.04
0.66	1.06	0.653	0.99	0.769	1.04
0.421	0.75	0.30	0.66	0.385	0.68

Freezing Point Lowering

Key { □ - C silicate
      ○ - D   "
      x - E   "

Normality in Terms of NaOH
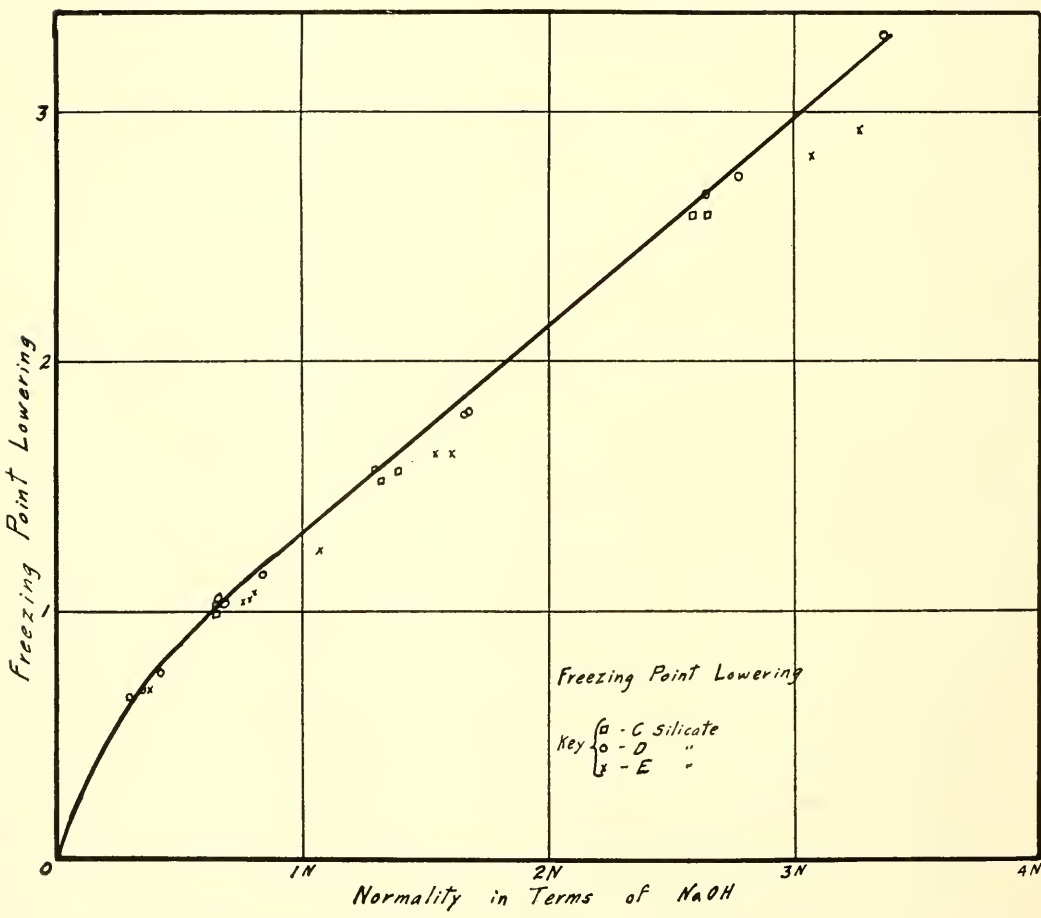
FIG. 8.—Thompson's Freezing Point Results.

Harman [65] studied freezing point depressions much more thoroughly with the following results:

TABLE 18. *Freezing Point Measurements.*

Wt. Normality	Molality	Observed Lowering	Molecular Depression	$i = \dfrac{\Delta *}{m X 1.858}$		
			$\dfrac{\Delta}{m}$			Kahlenberg and
N_w	m	Δ		Harman	Loomis	Lincoln
Ratio 1 : 1						
2.435	1.217	4.290	3.525	1.89	. . .	. . .
1.062	0.531	2.160	4.067	2.18	2.1	. . .
0.204	0.102	0.548	5.370	2.88	2.8	2.9
0.100	0.050	0.291	5.820	3.13	3.1	3.4
0.05	0.025	0.155	6.600	3.55	3.4	3.7
0.02	0.010	0.070	7.00	3.75	3.5	3.7
0.01	0.005	0.036	7.20	3.87	. . .	. . .
Ratio 2 : 1						
0.796	0.398	2.225	5.59	3.0	. . .	. . .
0.398	0.199	1.195	5.97	3.2	. . .	. . .
0.159	0.079	0.495	6.26	3.35	. . .	. . .
0.0796	0.0398	0.3002	7.54	4.0	. . .	. . .
0.0398	0.0199	0.170	8.45	4.5	. . .	. . .
0.0159	0.0079	0.080	10.12	5.4	. . .	. . .
Ratio 1 : 2						
2.450	1.225	2.140	1.747	0.94	. . .	. . .
1.100	0.550	1.215	2.209	1.94	. . .	. . .
0.500	0.250	0.770	3.080	1.65	. . .	. . .
0.204	0.102	0.415	4.068	2.19	. . .	. . .
0.100	0.050	0.255	5.100	2.74	. . .	. . .
0.050	0.025	0.140	5.600	3.01	. . .	. . .
0.020	0.010	0.060	6.000	3.22	. . .	. . .
0.010	0.005	0.033	6.600	3.55	. . .	. . .
Ratio 1 : 3						
2.00	1.00	1.465	1.465	0.772	. . .	. . .
1.00	0.50	0.985	1.970	1.06	. . .	. . .
0.50	0.25	0.680	2.720	1.46	. . .	. . .
0.20	0.1	0.405	4.050	2.17	. . .	. . .
0.10	0.05	0.220	4.400	2.36	. . .	. . .
0.05	0.025	0.130	5.200	2.73	. . .	. . .
0.02	0.01	0.055	5.500	2.96	. . .	. . .
0.01	0.005	0.030	6.000	3.22	. . .	. . .
Ratio 1 : 4						
2.00	1.00	1.050	1.050	0.565	. . .	. . .
1.00	0.50	0.795	1.590	0.855	. . .	. . .
0.50	0.25	0.540	2.160	1.16	. . .	. . .
0.20	0.10	0.340	3.400	1.83	. . .	. . .
0.10	0.05	0.215	4.300	2.31	. . .	. . .
0.05	0.025	0.125	5.000	2.69	. . .	. . .
0.02	0.01	0.055	5.500	2.96	. . .	. . .
0.01	0.005	0.028	5.600	3.01	. . .	. . .

$$* \Delta = \frac{\text{Molecular depression}}{\text{Molal lowering at infinite dilution for ideal substance}}$$

[65] *J. Phys. Chem.*, **31**, 355-373 (1927).
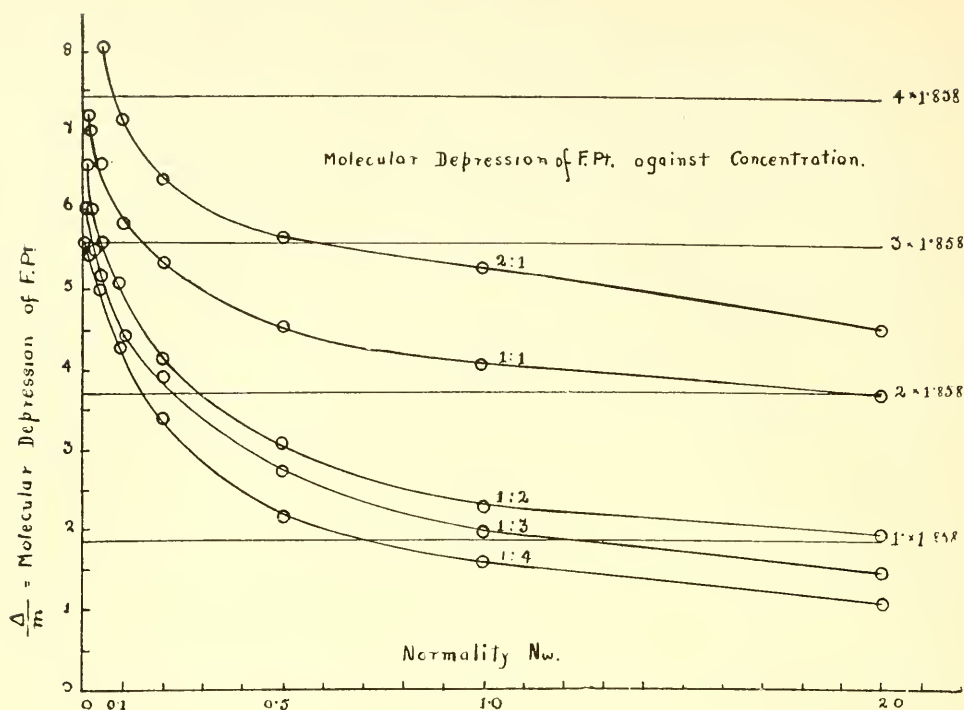
FIG. 9.—Molecular Depression of Freezing Point against Concentration.

Vapor Pressures. Lowering of the vapor pressure of water by silicate solutions of ratios 1:1 and 1:2 was also studied by Harman.[66]

TABLE 19. *Vapor Pressures at 25°C.*

N_w	Mean Exptl. Lowering	Calc'd Lowering if No Dissociation	Exptl. Lowering—Calc'd Lowering
		Ratio 1:1	
2.427	1.06 mm.	0.5096 mm.	2.08
1.062	0.55	0.2230	2.46
0.41	0.29	0.08610	3.36
0.102	0.08	0.02142	3.73
		Ratio 1:2	
2.0	0.45 mm.	0.42 mm.	1.08
1.0	0.31	0.21	1.49
0.5	0.20	0.105	1.90
0.2	0.10	0.042	2.38
0.1	0.055	0.021	2.61

Bennett [67] extended the work on vapor pressures by means of the dew point method.

[66] *J. Phys. Chem.*, **30**, 917-924 (1926).
[67] *J. Phys. Chem.*, **31**, 890-896 (1927).
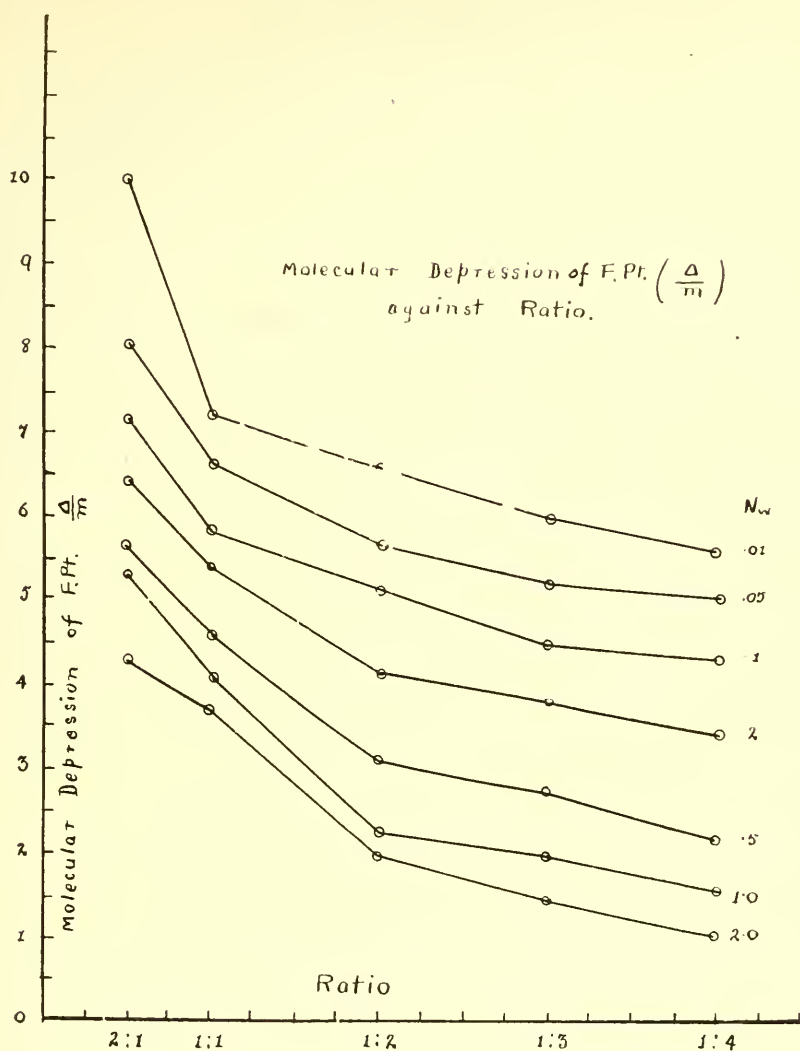
FIG. 10.—Molecular Depression against Ratio.

TABLE 20. *Dew Point Lowerings in Degrees Centigrade.*

M^x	NaOH ...	1:0.5	1:0.87	Ratio Na$_2$O to SiO$_2$ in Silicates 1:1	1:1.4	1:2	1:3.2	1:3.95
1.5	2.40	1.74	...	1.35	1.06	0.75	0.48	0.41
1.0	1.51	1.19	0.88	0.92	0.74	0.56	0.35	0.29
0.5	0.75	0.60	0.46	0.46	0.37	0.30	0.19	0.15
0.3	0.45	0.37	0.28	0.28	0.22	0.19	0.12	0.10
0.2	0.29	0.25	0.19	0.19	0.14	0.13	0.08	0.07

^{x} = gram mols of Na$_2$O per 1000 grams of water.

Boiling Points.   Cann,[68] Cheek, and Gilmore [69] worked on boiling point determinations of solutions of sodium silicate and found a direct relationship between the soda and silica content and the elevation of the boiling point.

[68] Cann, Jessie Y., and Dorothy L. Cheek, *Ind. Eng. Chem.*, **17**, 312 (1925).
[69] Cann, Jessie Y., and Gilmore, *J. Phys. Chem.*, **32**, 72 (1928).
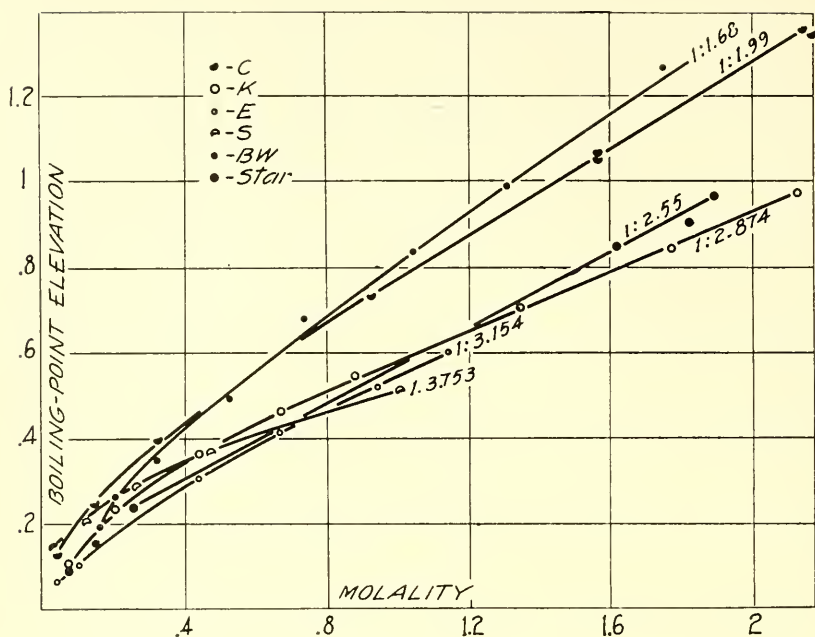
Fig. 11.—Boiling Point Elevations.

Table 21. *Boiling Point Elevation of Silicate Solutions.*

Na_2O, $1.68SiO_2$		Na_2O, $2.06SiO_2$		Na_2O, $2.55SiO_2$	
Per Cent Soda Content	Boiling Point Elevation at 760 Mm.	Per Cent Soda Content	Boiling Point Elevation at 760 Mm.	Per Cent Soda Content	Boiling Point Elevation at 760 Mm.
0.556	0.086	0.316	0.1276	0.476	0.097
0.685	0.124	0.316	0.1243	0.849	0.177
0.708	0.025	0.421	0.1567	1.074	0.199
0.823	0.160	0.946	0.2463	1.463	0.236
0.897	0.073	0.947	0.2453	7.359	0.897
0.933	0.137	1.136	0.2723	8.054	0.854
1.046	0.141	1.170*	0.2531	8.293	0.961
1.100	0.189	1.933	0.3936		
1.204	0.258	1.888	0.3819		
1.900	0.345	4.874	0.7334		
3.010	0.495	7.486	1.0578		
4.039	0.678	7.508†	1.0721		
5.490	0.835	9.516‡	1.3617		
6.650	0.991	9.540	1.3480		
8.390	1.269				
9.752	1.475				

* Uneven pumping in silicate apparatus due to insufficient heat.
† Uneven pumping in water apparatus.
‡ Uneven pumping in silicate apparatus probably due to viscosity of solution.

TABLE 21. *Boiling Point Elevation of Silicate Solutions—(Continued).*

Na₂O, 2.96SiO₂		Na₂O, 3.25SiO₂		Na₂O, 3.87SiO₂	
Per Cent Soda Content	Boiling Point Elevation at 760 Mm.	Per Cent Soda Content	Boiling Point Elevation at 760 Mm.	Per Cent Soda Content	Boiling Point Elevation at 760 Mm.
0.109	0.0639	0.307§	0.0707	0.143	0.1013
0.223	0.0993	0.309§	0.0627	0.143	0.0937
0.495	0.1230	0.611§	0.1071	0.498	0.1490
0.809	0.1743	0.637§	0.1207	0.497¶	0.1629
1.241	0.2272	1.122	0.1960	0.762	0.1986
1.253	0.2246	1.122	0.1902	0.778	0.1932
2.472	0.3625	2.433	0.3027	1.512	0.2828
2.466	0.3550	2.455	0.3051	1.495	0.2834
3.550	0.4529	3.553‖	0.4122	2.571	0.3664
3.502	0.4579	3.553‖	0.3905	2.572	0.3730
4.511	0.5361	4.783‖	0.5082	3.479	0.4223
4.416	0.5434	4.706‖	0.5183	4.577	0.5067
5.942	0.6856	5.467‖	0.5970		
5.982	0.6865				
7.456	0.8394				
8.638	0.9659				

§ Per cent by volume.
‖ Large amount of frothing occurred.
¶ Used new apparatus for water which did not pump well.
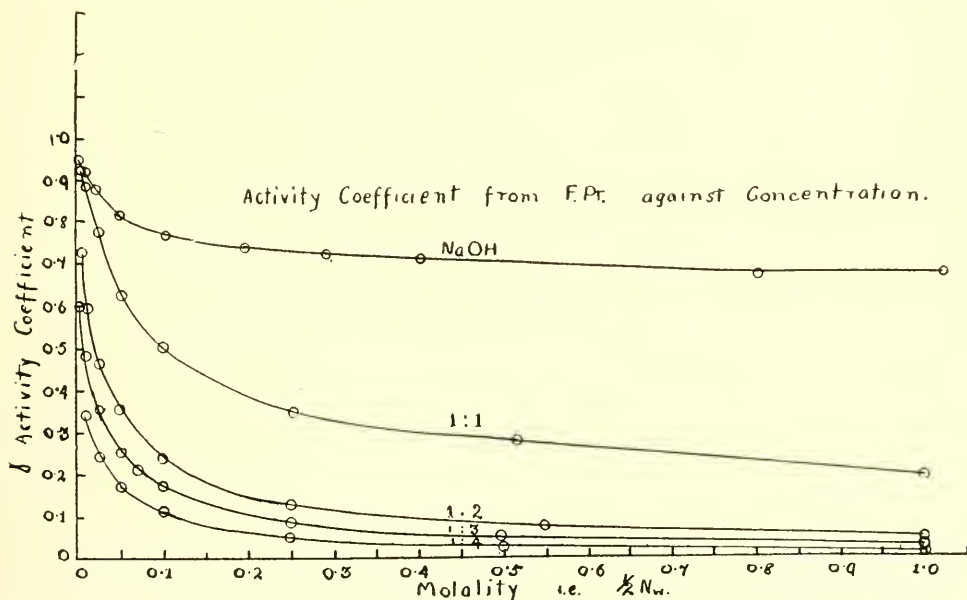
FIG. 12.—Activity Coefficient against Concentration.

Activity Coefficients. Calculation of activity coefficients from his vapor pressure and freezing point depressions led Harman to the following conclusions:

"From the results it appears that ratio 1:1 is the salt Na_2SiO_3 undergoing both hydrolytic and ionic dissociation giving rise to Na^+, OH^-

and SiO_3^{--} ions and H_2SiO_3, most of the latter being crystalloidal. Na_2SiO_3 is practically completely dissociated in dilute solution, but only 27.8 per cent hydrolytically. Ratio $1:2$ is the definite salt $NaHSiO_3$, behaving like Na_2SiO_3 and giving rise to Na^+, OH^- and $HSiO_3^-$ ions
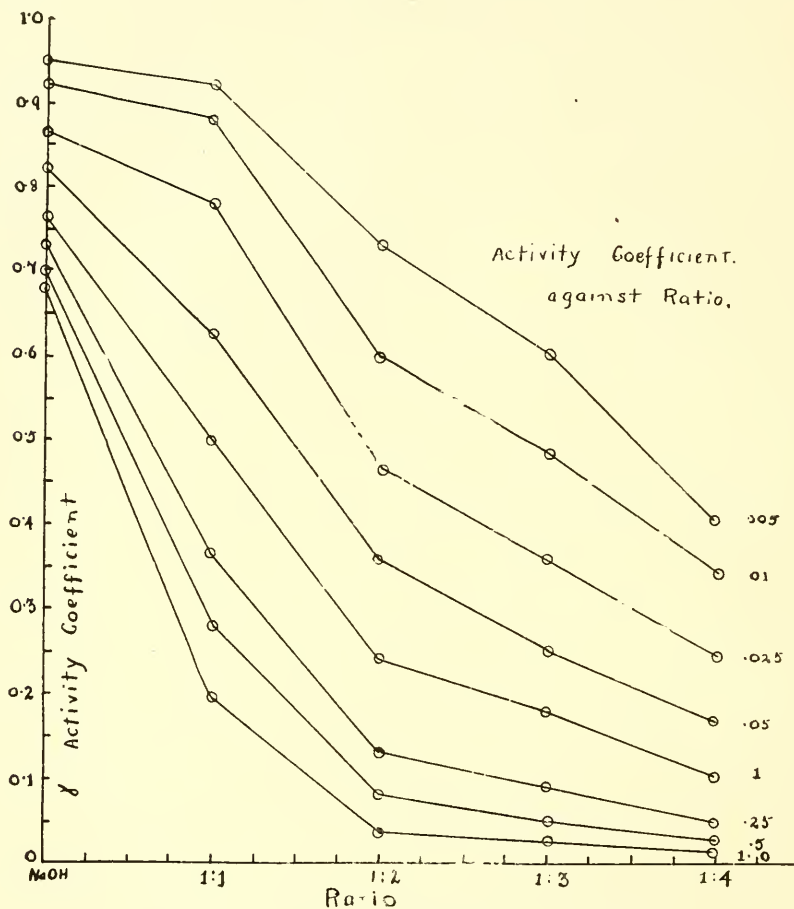
FIG. 13.—Activity Coefficient against Ratio.

and H_2SiO_3. There is 0.60 per cent dissociation at concentration 0.005 m but only 0.05 per cent hydrolytic dissociation. The results from ratios $1:3$ and $1:4$ are not in accord with the view that these ratios are definite salts but agree well with the existence of complex aggregates in concentrated solution and of ionic micelles of the composition (m SiO_3 n SiO_2 aq.)$^{m-}$ where $m + n/m =$ ratio; the following equilibrium also existing :

$$SiO_3^{--} + (Colloid\ SiO_2\ aq.)\ (mSiO_3.n\ SiO_2\ aq)^{m--}$$
$$(Colloid\ SiO_2\ aq.)\ crystalloid\ H_2SiO_3\ 2H + SiO_3^{--}."$$
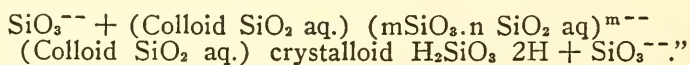
Activity coefficients calculated from vapor pressure and dew point measurements by Bennett are in close agreement with the foregoing.

Harman and Bennett [70] both used $v = 4$ in the equation

$$J = 1 - \frac{\Delta}{v \lambda m}$$

in order to get comparable and reasonable results for all ratios of Na_2O to SiO_2 in the range covered. Randall and Cann [71] point out that "their (Harman's and Bennett's) calculations tacitly assume for the reaction

$$Na_2SiO_3 \text{ (Aq.)} + H_2O \text{ (1)} = 2Na^+ + OH^- + HSiO_3^- \qquad (4)$$
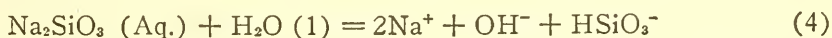
$K = 1$, in accordance with the conventions adopted by Lewis and Randall in developing the basic equations used. In other words, the
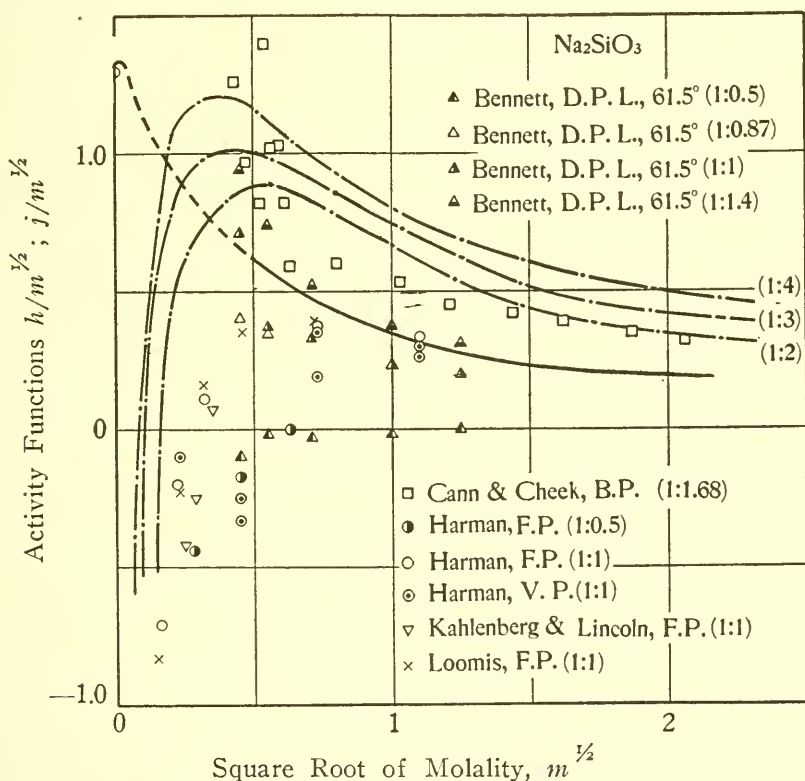
Fig. 14.—Activity Function of Sodium Metasilicate.

activity of the sodium silicate is made equal to the geometric product of the activities of the ions on the right of Equation 4." Randall and Cann used "$v = 3$ for ratios of $1:1$ of Na_2O to SiO_2 and $v = 2$ for ratios of $1:2$ to $1:5$. In the latter case, the molality was taken equal to the number of gram atoms of sodium ion constituent. These assumptions correspond to $K = 1$ for the reactions:

$$Na_2SiO_3 \text{ (aq.)} = 2Na^+ + SiO_3^{--} \qquad (5)$$
$$NaHSiO_3 \text{ (aq.)} = Na^+ + HSiO_3^-. \qquad (6)$$
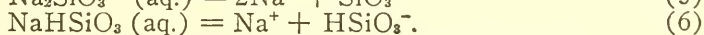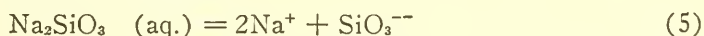
[70] Lewis and Randall, "Thermodynamics," Equation 2, 1923, p. 342.
[71] Randall, Merle, and Jessie Y. Cann, *J. Am. Chem. Soc.*, **50**, 347 (1928).

It has been impossible to eliminate the effect of hydrolysis, but in the concentrated solutions, this effect cannot be large, and the method of extrapolation here used eliminates to a large extent the effect in the more dilute solutions." The results of these calculations are given in Figure 14 and the values for the activity coefficients in Table 22.

TABLE 22. *Activity Coefficients of Sodium Silicate Solutions (0-100°C.).*

Molality	Na_2SiO_3	$Na_2O, 2SiO_2$
0.05	0.501	0.464
0.10	0.408	0.347
0.20	0.322	0.246
0.50	0.232	0.131
1.00	0.182	0.076
2.00	0.141	0.043
4.00		0.027

The low values obtained for the more silicious silicates are explained on "the assumption of the existence of micelles, which are not entirely dissociated except in very dilute solutions." The assumption may be made that the size and number of micelles is less in solutions containing relatively less silica. The charge of the micelle will then be greater, the greater the silica content of the negative constituent.

"In a very real sense, the assumption that the ions existing in acid silicate solutions are $Si_2O_5^{--}$ or some hydrated multiple thereof, may be considered as the first stage in the formation of a micelle, for undoubtedly the negative constituent consists of many different sorts of micelles all in equilibrium (more or less rapid) with each other. But, as we do not have a method of picking out the concentrations of the individual species of micelles, we may as well take $HSiO_3^-$ just as we do in the case of water, when we choose H_2O as the species to represent this substance.

"All the micelles referred to have been considered to be ionic micelles. McBain and Salmon [72] postulate both ionic and neutral micelles. . . . There has been no suggestion of the separate existence of neutral micelles in the silicate solutions."

Sodium-Ion Activity. Harman [73] determined the sodium-ion activity by means of a sodium amalgam electrode. The results are given in Figure 15.

"The values for the activity coefficient of Na_2SiO_3 show that in concentrated solution as much as 40 per cent of the total sodium exists in active ionic state, while in dilute solution practically all the sodium

[72] *J. Am. Chem. Soc.*, **42**, 426 (1920).
[73] *J. Phys. Chem.*, **30**, 917-924 (1926).

exists so. The coefficient for ratio 1 : 1 passes through a minimum at concentration 0.2 N_w, while none of the other ratios exhibit such a minimum. It is not unusual to find this minimum for strong electrolytes in concentrated solution.
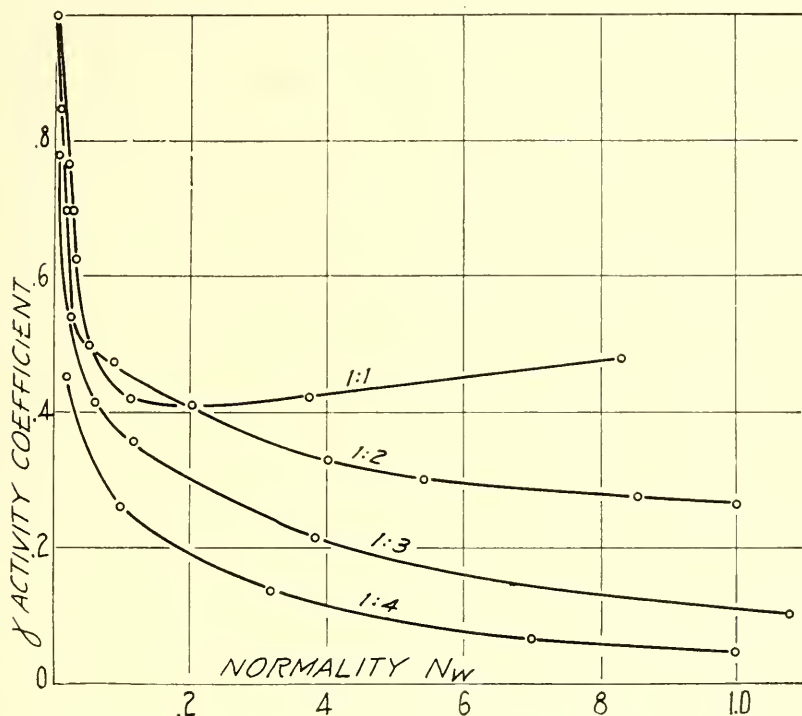
Fig. 15.—Sodium-Ion Activity against Concentration.

"In ratio 1 : 3 and 1 : 4, the values are very low in concentrated solution and even in dilute solution are still comparatively low, indicating that all the sodium in solution does not exist as sodium ion, or if so, the silica present has considerably affected and reduced its activity."

Diffusion Through Membranes. Additional support for the foregoing evidence of the presence of silicate ions was obtained by Ganguly [74] and by Harman [75] from diffusion experiments using collodion and parchment membranes.

The relative instability of collodion films in silicate solutions renders results with membranes of this material open to serious question. Both found that equilibrium was reached in about a week.

"All ratios at all concentrations gave evidence of diffusion of sili-

[74] Ganguly, *J. Phys. Chem.*, **31**, 407-416 (1927).
[75] Harman, *op. cit.*, 623-625.

cate ions both with the collodion membrane and with parchment paper. . . . With ratios of $1:1$ and $1:2$ equal distribution of both sodium and silica was found to have taken place with a $0.3 N_w$ solution."

Here certainly is definite proof of the crystalloid nature of silicates of these ratios in dilute solution. Harman found "about 2/3 of the silica in $0.3 N_w$ $1:4$ and about 1/3 in $1.0 N/w$ H_2SiO_3 was crystalloidal." He points out that investigators of silicic acid should take cognizance of this fact and not prepare their material by dialysis.

Ganguly worked with the ratios above $1:2$.

TABLE 23. *Analyses After Equilibrium with Parchment Paper.*

Molar Ratio	Silicate Compartment		Water Compartment		Difference	
	SiO_2 Gms. per 100 cc.	Na_2O Gms. per 100 cc.	SiO_2 Gms. per 100 cc.	Na_2O Gms. per 100 cc.	SiO_2	Na_2O
4.2	1.8930	0.399	1.107	0.335	0.786	0.064
3.95	1.8024	0.4238	1.1908	0.3648	0.6116	0.059
3.8	1.6996	0.4308	1.2942	0.3806	0.4054	0.0502
3.3	1.6308	0.4802	1.3664	0.4548	0.2644	0.0254
3.0	1.5254	0.5192	1.4734	0.5090	0.052	0.0102
2.5	1.5372	0.6236	1.4752	0.6140	0.062	0.0096
2.0	1.5074	0.766	1.4918	0.7748	0.0156	—0.0088

TABLE 24. *Analyses After Equilibrium with Collodion Membranes.*

Molar Ratio $\frac{SiO_2}{Na_2O}$	Silicate Compartment		Water Compartment		Difference	
	SiO_2 Gms. per 100 cc.	Na_2O Gms. per 100 cc.	SiO_2 Gms. per 100 cc.	Na_2O Gms. per 100 cc.	SiO_2	Na_2O
4.2	1.1094	0.2062	0.3968	0.1624	0.7126	0.0438
3.95	1.0478	0.2172	0.4608	0.1748	0.5870	0.0424
3.8	0.9298	0.2246	0.5776	0.1834	0.3522	0.0412
3.3	0.8788	0.2524	0.6294	0.2176	0.2494	0.0348
3.0	0.7736	0.2640	0.7332	0.2524	0.0404	0.0116
2.5	0.7722	0.3178	0.7338	0.3022	0.0384	0.0156
2.0	0.7568	0.3852	0.7496	0.3896	0.0072	—0.0044

"The distribution was greatly dependent on the original molar ratios of the solutions. Solutions up to the molar ratio $1:3$ showed very little variations in concentrations during diffusion, showing thereby that the quantity of non-diffusible matter in those solutions was comparatively small.

"The quantity of non-diffusible matters increased very rapidly after the ratio $1:3$. This result is quite in line with the previous measurements on the light-scattering of the silicate solutions,[76] and shows beyond doubt that after the ratio $1:3$, the quantities of colloidal matter

[76] Ganguly, *J. Phys. Chem.*, **30**, 706 (1926).

in the silicate solutions increase at a very rapid rate. . . . Measurements of pH of the solutions after equilibrium showed that hydrolysis does not take any prominent part during these distribution processes." The osmotic pressures also indicated an increase of colloidal matter with ratio.

CHEMICAL EVIDENCE.

Colorimetric Reaction with Crystalloidal Silica. A colorimetric test for crystalloidal silica was used by Harman [77] to give still further evidence of silicate ions. This test depends upon the formation of a greenish yellow silicomolybdate.[78] Though less convincing than the transport measurements it is interesting to note that this test seems to show that in dilute solutions most of the silica is crystalloidal but with rising concentration, first in the higher ratios, the colloidal content is

FIG. 16.—Molar Ratio.

increased. The color produced by a given normality of the ratio in question was matched with a solution of ratio 1:1 whose normality was determined. From these figures the ratio of crystalloidal silica in the two solutions was determined as shown in the third, sixth, and last columns of the following table:
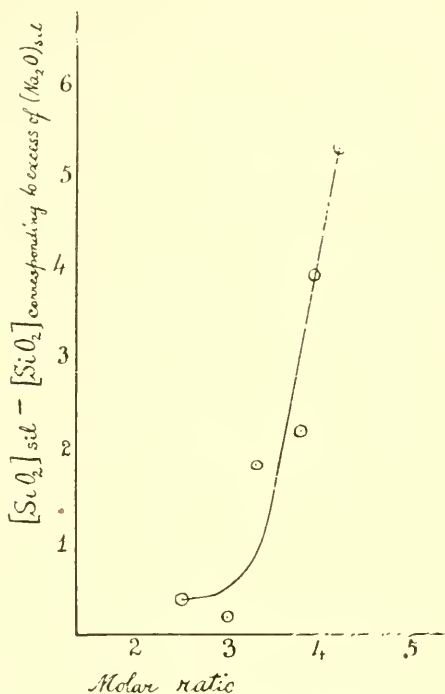
TABLE 25. *Colorimetric Test.*

Na_2O 2:1	Normality Std. 1:1	Crys. sil. in 2:1 / Crys. sil. in 1:1	Std. 1:1	$\dfrac{1:3}{1:1}$	1:4	Std. 1:1	$\dfrac{1:4}{1:1}$
0.0005	0.00025	0.5	0.0005	0.0015	3.9	0.0005	0.002	4.0
0.001	0.0005	0.5	0.001	0.0025	2.8	0.001	0.004	4.0
0.002	0.001	0.5	0.003	0.009	3.0	0.003	0.010	3.3
0.003	0.0015	0.5	0.005	0.014	2.8	0.005	0.016	3.2
0.004	0.002	0.5	0.007	0.018	2.6	0.007	0.022	3.1

"It is seen that in very dilute solution, 0.0005N, ratio 1:4, contains as much crystalloidal silica as 0.002N, 1:1, the normalities in accord-

[77] *J. Phys. Chem.,* **31**, 622-623 (1927).
[78] Dienert and Waldenbulcke, *Compt. rend.,* **176**, 1478 (1923); *Bull. Soc. Chim.,* **33**, 1131-1140 (1923).

ance with the practice adopted in this investigation being expressed in terms of the sodium content. In other words, practically all the silica in ratio 1 : 4 exists in the crystalloidal state at a dilution of 0.005N, or more correctly, ratio 1 : 4 contains 4 times as much crystalloidal silica as ratio 1 : 1 at this dilution.

"Similarly at this dilution, all the silica in ratios 2 : 1 and 1 : 3 exists in the crystalloidal state.

"As the solution gets more concentrated we see that ratio 1 : 4 no longer contains 4 times as much crystalloidal silica as ratio 1 : 1, indicating that in the more concentrated solutions some of the silica in ratio 1 : 3, and still more in ratio 1 : 4, passes into the colloidal state.

"Hence in extremely dilute solutions of these ratios practically all the silica exists in the crystalloidal state, but with increasing concentration increasing amounts of colloidal silica are manifested."

Electrometric Titrations. Stericker [79] titrated sodium silicate solutions electrometrically and found breaks at points suggesting the

Fig. III A

Electrometric Titration of
Sodium Silicate Solution
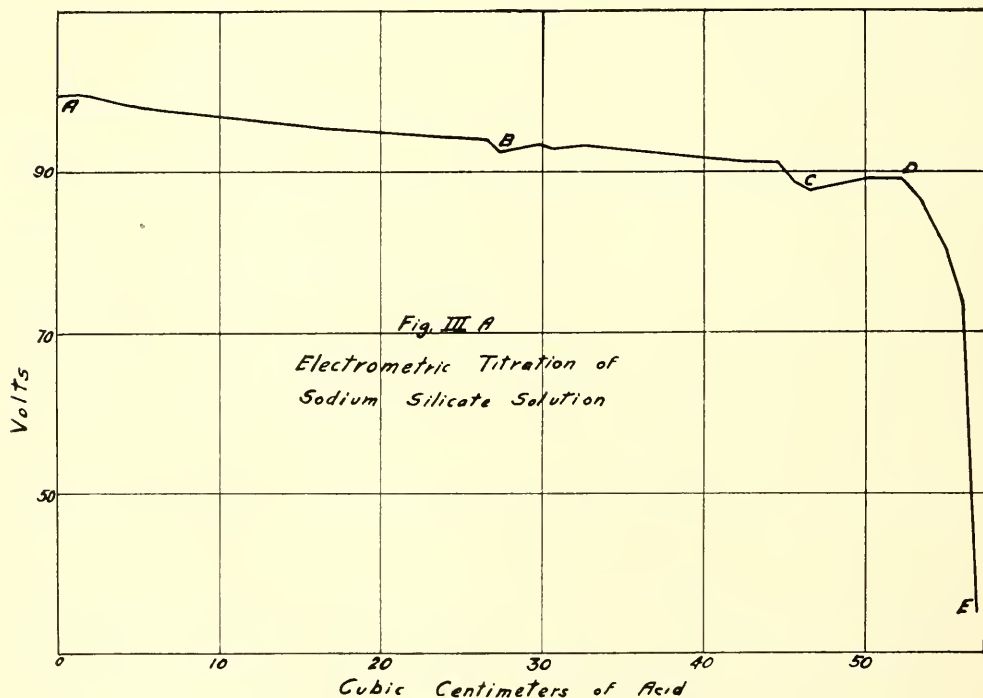
Fig. 17.

presence of $Na_2Si_2O_5$ and Na_3SiO_3. Harman [80] also made titrations of this kind on entirely different solutions and came to similar conclusions.

[79] Stericker, Wm., Doctor's Thesis, University of Pittsburgh (1922).
[80] *J. Phys. Chem.*, **31**, 616-622 (1927).

Conclusions. All the results indicate that solutions of the sodium silicates contain much less colloidal material than has commonly been believed. Simple and complex silicate ions are present; they remove the discrepancy between the earlier views of complete hydrolysis and hydrogen-ion measurements. Although the exact nature of the silicate solutions has not been completely explained, a substantial advance has been made in the last few years.

Harman [81] has given the following summation of our present knowledge of these solutions.

"Silica exists in solutions of these ratios not wholly colloidal as heretofore supposed, but wholly or partly as crystalloidal silica depending upon the ratio $Na_2O : SiO_2$, and upon the concentration. This crystalloidal silica exists in equilibrium with silicate ions, or electrically charged aggregates, of silicate ions and silica, i.e., ionic micelles, or pure colloidal aggregates, as the case may be, depending upon the ratio and concentration.

"In aqueous solution at 25°C. two and only two salts, viz., Na_2SiO_3, i.e., ratio 1:1, and $NaHSiO_3$, i.e., ratio 1:2, appear to exist as such, the behavior and nature of which are now elucidated.

"Ratios other than 1:1 and 1:2 are not definite salts but are typical examples of colloidal electrolytes.

"The fundamental nature of silica in solution appears to depend upon the existence, at least in the range here investigated, of only one acid, metasilicic acid, in which the equilibrium between the crystalloidal and the colloidal constituents depends upon the concentration, the crystalloidal content at ordinary concentrations being much greater and the acid, therefore, much stronger, than generally supposed."

Structure of Systems With Relatively Low Water Content.

Exchange Properties. When sodium has been adsorbed on colloidal silica, it reduces but does not entirely destroy the tendency of the particles to coalesce. Silicate solutions in which the ratio of silica to sodium is above 4.2 are unstable. They tend to gel on standing, and solutions of much lower ratio are easily thrown out of equilibrium by the removal of part of the alkaline content by neutralization, by dialysis, or by electrolysis. A gel made by the partial neutralization of a sodium silicate solution will undergo exchange reactions in which the adsorbed sodium is replaced by adsorbed calcium from any soluble calcium salt. Sodium may be replaced by treating the calcium gel with

[81] *J. Phys. Chem.,* **32,** 44 (1928).

a solution of a soluble sodium salt of sufficient concentration to reverse the equilibrium. Wheaton's formation of a gel for water softening [82] is based on this principle.

Effect of Age on Viscosity. There is a tradition that industrial silicate solutions tend to increase in viscosity with age. This is always observed on long standing of silicates having ratios of $3SiO_2$, Na_2O or more, when stored in glass bottles or even when hermetically sealed in a glass tube. Storage of five years' duration in iron bombs showed that adhesive silicates do not change in viscosity within the limits of measurements made with the Stormer viscometer during such a period. The familiar thickening must be attributed to loss of moisture or to a reaction with the containing vessel which reduces the protective action of the adsorbed sodium on the silica particles.

Structure in Concentrated Solutions. With the increase of alkali metal the concentrated solutions depart from the physical characteristics of gels, which are quite evident in solutions of the composition $Na_2O, 3SiO_2$ and those with larger amounts of silica. Such solutions may be concentrated to a point where they appear to be solids. Under sudden stress, they break with a conchoidal fracture. They show elastic properties, for though they can easily be molded in the hand, they will bounce like a rubber ball, but if allowed to stand, they will flow under the slightest pressure. Determinations of their stress-flow curves show that these pass to the zero point; they are viscous liquids and not, like suspensions of clay, which remain immovable up to a critical stress, plastic solids.[83] What, then, is the explanation of the bouncing ball of concentrated silicate? Until a better explanation is forthcoming, the idea that colloidal silica has begun to form a gel structure which it is unable to complete due to the viscous character of the liquid phase, seems to satisfy the requirements. Then we might have a liquid free to move in the interspaces of the loosely formed gel which, continually tending to reconstruct itself, would push it back toward its original position and yet not be strong enough to resist the tendency to flow under very slight pressure, operating through a considerable period of time.

ADSORPTION OF SODIUM IONS ON SILICA PARTICLES.

Experimental evidence tending to show the adsorption of sodium ions on silica particles has been obtained in a large number of cases.

[82] Brit. Pat. 142,974 (1920).
[83] Bingham and Jacques, *Chem. & Met. Eng.*, **28**, 727 (1923).

Jordis,[84] working on the precipitation of ferric chloride by sodium silicate, obtained precipitates of strong alkaline reaction and supernatant liquors which were strongly acid although the amounts of sodium and chlorine in the solutions mixed were in a stoichiometrical relation. The sodium was so firmly attached to the colloidal particles of silica that it was actually removed from solution. A rather extended experience with precipitates from silicate solutions, as, for instance, the precipitate formed with aluminum sulfate in sizing paper with sodium silicate, justifies the statement that these precipitates always carry alkali with them out of solution in a form which requires prolonged washing for its removal. Some recent studies on a steam boiler operating on a closed circuit with high-grade distilled water showed a steady decline of both sodium and silica content after the addition of sodium silicate put into the system to control corrosion.[85]

In all cases where silica is separated from an alkaline solution either as an amorphous precipitate or gel, some of the base is carried with it. This takes place under such widely differing circumstances as the separation of films from dilute solutions and the precipitate of silica and stannic phosphate adsorbed on silk fibers in the process of weighting.

Although colloidal silica is present in all silicate solutions of industrial importance, its behavior does not alone account for all their properties. The bouncing ball of concentrated silicate solution contains in addition to its incipient structure a fluid phase in the interspaces. We have here to do not only with colloidal systems but with salt solutions the exact nature of which remains to be explored.

[84] *Z. angew. Chem.,* **19**, 1697-1702 (1906).
[85] Hecht, Max, personal communication.

Chapter III.

Definite Soluble Silicates.

Sodium Silicates.

The composition of soluble silicates is not bounded by the limits implied by the formulas of definite compounds which may be separated and studied. In dilute solutions the silica and base may be present in any proportions. These solutions have characteristics which distinguish them from those of all other alkaline salts. From some of them definite crystalline bodies may be obtained, while others remain viscous and glue-like and yield no compounds which can be separated as crystals or otherwise identified as chemical individuals. Each ratio yields, however, a set of reproducible properties of widely varied character as we progress from one end of the series to the other. The compounds which may exist in solution, as well as the nature of the silica or alkali above the amounts thus accounted for, are matters of consequence if we would understand the behavior of silicate solutions in industry.

Formation of Hydrous Forms of Metasilicate.

If a solution containing equi-molecular proportions of Na_2O and SiO_2 be concentrated to a water content of 50 per cent and allowed to stand at ordinary temperatures, crystalline sodium metasilicate will be formed. This salt was first reported by Fritzsche,[1] who described two hydrates, $Na_2SiO_3 . 6H_2O$ in monoclinic crystals, and $Na_2SiO_3 . 9H_2O$ in rhombic. Subsequent workers reported crystalline sodium metasilicates with five,[2] seven,[3] ten,[4] and twelve [5 and 6] molecules of water but it is probable that these were mixtures of other hydrates, more or less decomposed.

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[1] Fritzsche, *Poggendorf's Ann. der Physik und Chem.,* **131**, N.S. **43**, 135-138 (1838).

[2] Peterson, Theodor, *Ber.,* **5**, 409 (1872) ; also *J. pr. Chem., N.F.S.,* 397 (1892).

[3] Yorke, *Phil. Trans. Roy. Soc.,* **147**, 533 (1857).

[4] Mylius, F. and F. Foerster, *Ber.,* **22**, pt. 1, 1092 (1888).

[5] Weber. See Gmelin-Kraut, "Handbuch der anorgischen Chemie," 7 Auflage, Bd. **3**, Abt. 1, pp. 222-223 and 229-234 (1909).

[6] Jordis, *Z. anorg. Chem.,* **56**, 305 (1907).

Vesterberg [7] prepared the ennehydrate $Na_2SiO_3.9H_2O$ by crystallizing from solutions containing alcohol and also reported the existence of a compound with $6H_2O$ from observations of the dehydration of the salt with $9H_2O$ over concentrated sulfuric acid and rehydrating over sodium hydroxide at specific gravity 1.26. Dehydration of $9H_2O$ over 50 per cent potassium hydroxide led him to believe

Fig. 18.—Sodium Metasilicate.
$Na_2SiO_3.4H_2O$
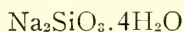
there is a hydrate with $3H_2O$ but later workers have not confirmed this.

In an effort to produce a silicate analogous to $NaHCO_3$, Jordis [8] obtained after long standing of the solution a crystalline mass which proved to be Na_2SiO_3. Finally the hexahydrate crystallized from a very alkaline solution.

The most complete studies of sodium metasilicates are those of Erdenbrecher,[9] who began his work at Erlangen under Jordis. He applied physico-chemical methods to determine what definite hydrates are

[7] Vesterberg, K. A., *Proc. 8th Int. Congress of Exp. Chem.*, **8**, 235 (1912).
[8] Jordis, E., *Chem. Ztg.*, **38**, 922 (1914).
[9] Erdenbrecher, A., *Chem. Ztg.*, **39**, 583 (1915); *Mikrokosmos*, **15**, 55-60 (1921); *Z. anorg. allgem. Chem.*, **124**, 339-354 (1922).
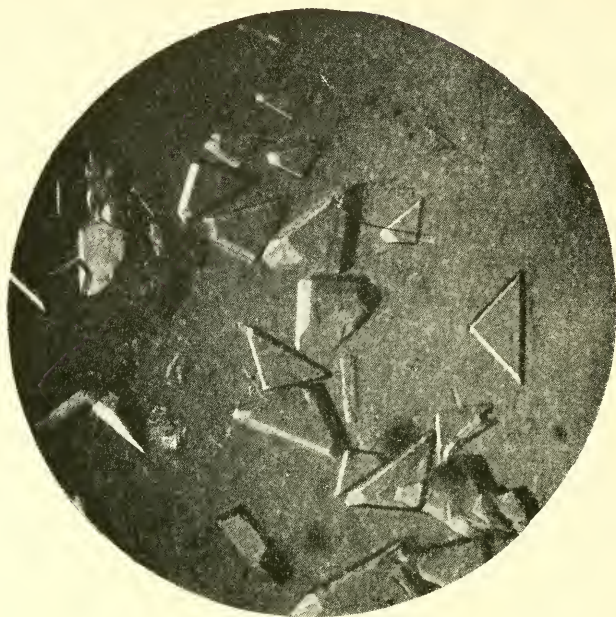
Fig. 19.—Sodium Metasilicate.
$Na_2SiO_3.6H_2O$

Fig. 20.—Sodium Metasilicate.
$Na_2SiO_3.9H_2O$

formed and then prepared and studied the crystalline forms containing four, six, and nine molecules of water.

With an apparatus like that shown in the cut the temperature of a water bath during heating and cooling was observed with one thermometer and the readings were plotted in comparison with those of a
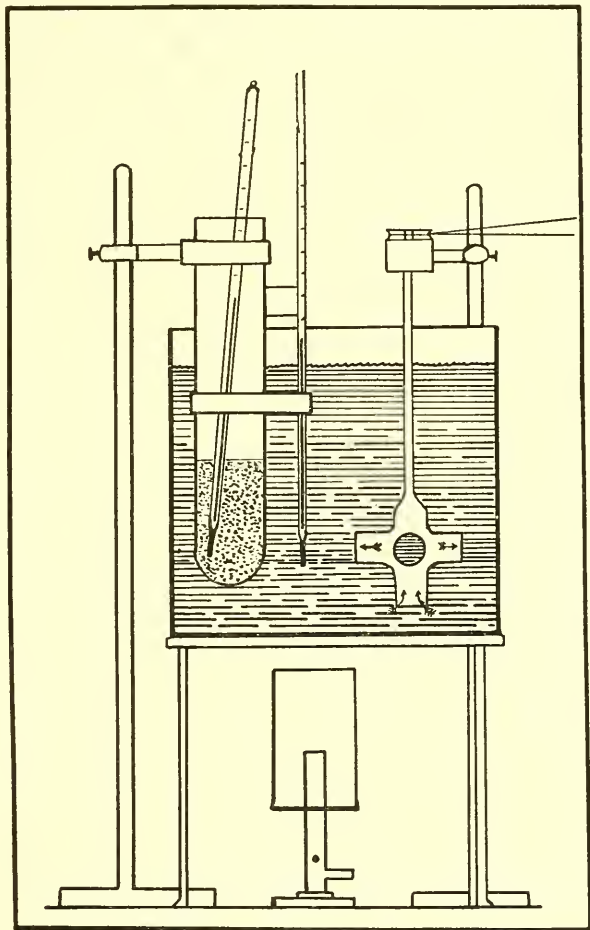
Fig. 21.—Erdenbrecher's Apparatus for Studying the Hydrates of Sodium Metasilicate.

thermometer immersed in the metasilicate in the test tube. As crystallization took place or crystals dissolved, alterations in the rate of thermal change in the silicate indicated the points at which definite hydrates formed and melted. Manipulation was difficult because the silicate crystals tended to set to a solid mass, but it was found that the addition of paraffin oil would keep them in a mushy condition so that they could be stirred with a thermometer, without invalidating the results.

The method was tested with sodium carbonate and sulfate and found to give results in accord with the known characteristics of these salts; the breaks in the time-temperature curves corresponded to the melting points of the crystal hydrates. With Na_2SiO_3, the manipulation was
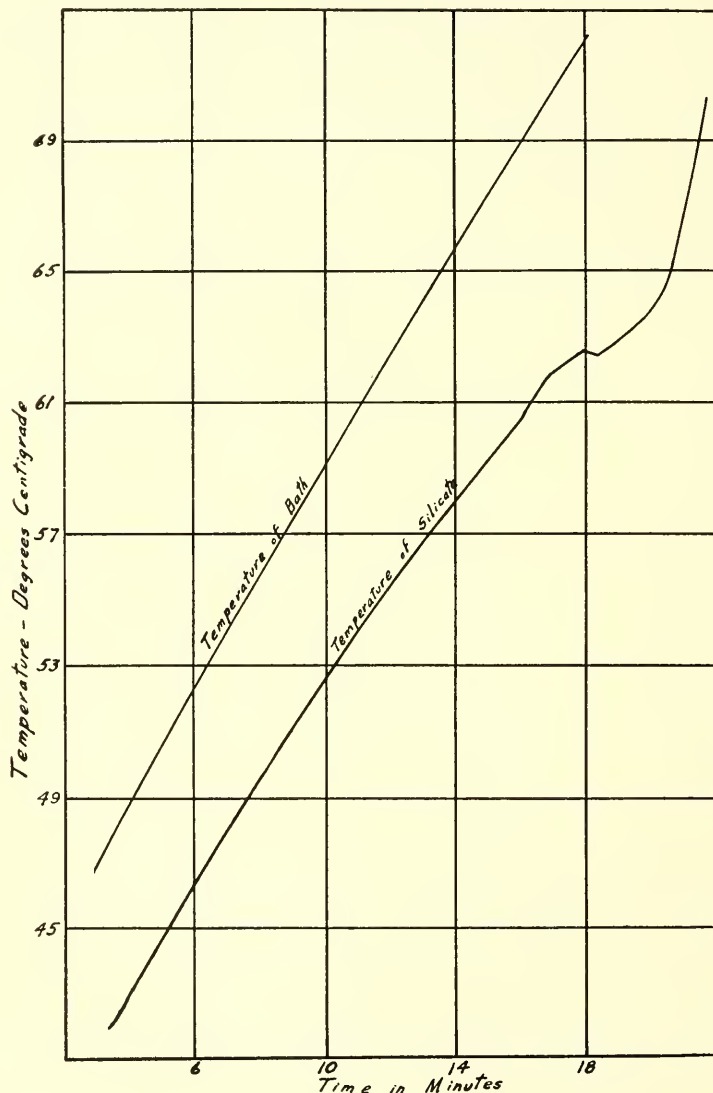
Fig. 22.—Cooling Curves of Sodium Metasilicate.
$Na_2SiO_3.6H_2O$

further complicated by the tendency to undercool without crystal formation and to crystallize so slowly that the temperature differences could not be observed. The solutions were seeded with metasilicate crystals and a technic was developed which showed the correct melting points of the three hydrates illustrated.

Na$_2$SiO$_3$. 9H$_2$O melts at 47°, crystals rhombic.
Na$_2$SiO$_3$. 6H$_2$O melts at 62.5°, crystals monoclinic.
Na$_2$SiO$_3$. 4H$_2$O melts about 85°, crystals hexagonal.

Studies of the vapor pressure of sodium metasilicate with 57.4, 58.6, 60.5, and more than 60.5 per cent water, showed a change at 37.2°C.
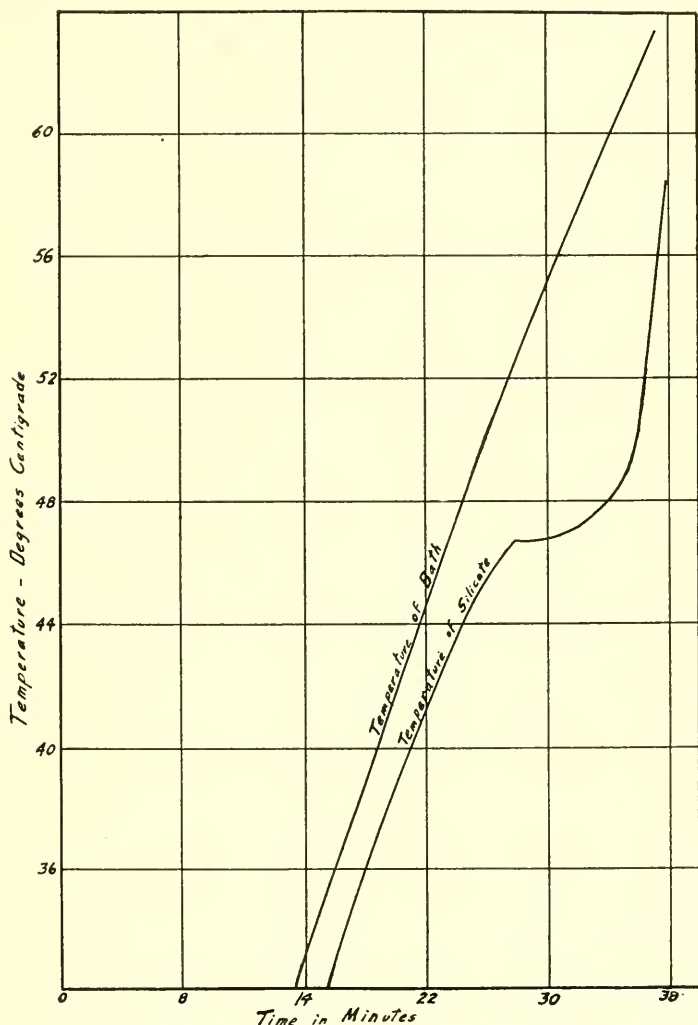
Fig. 23.—Cooling Curves of Sodium Metasilicate.
Na$_2$SiO$_3$.9H$_2$O

which is thought to be the melting point of Na$_2$SiO$_3$.14H$_2$O, but this salt has not been isolated.

The ennehydrate is the most easily prepared. Commercial metasilicate was found to contain 10H$_2$O, probably due to the presence of a mixture of hydrates more or less decomposed or to incomplete sepa-

ration of crystals and mother liquor. If 30 grams of the crude substance and 6 to 9 grams of sodium hydroxide were dissolved in 30 cc. of water, $Na_2SiO_3.9H_2O$ crystallized in beautiful long rhombic plates. With the sodium hydroxide increased to 18 grams the hexahydrate in well defined crystals was obtained while with 26 grams of sodium hydroxide on long cooling the product was $Na_2SiO_3.4H_2O$.

TRANSFORMATIONS OF HYDRATES.

By altering the amount of water or of sodium hydroxide in the mother liquor, a series of transformations from one crystal form to
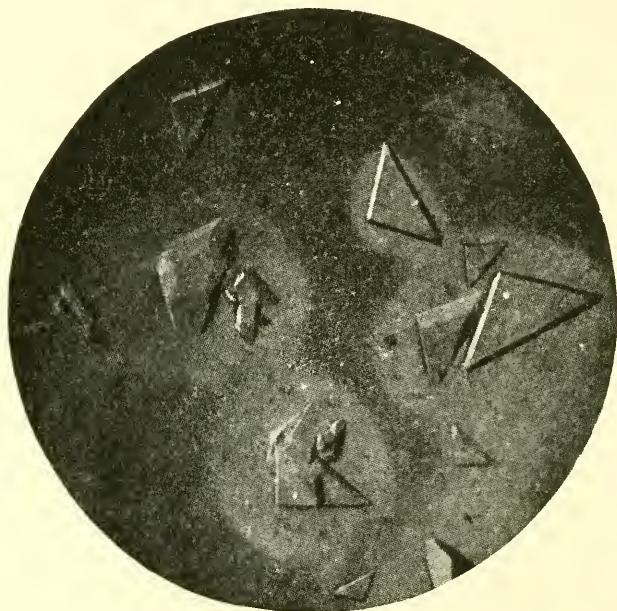
FIG. 24.—Sodium Metasilicate. Transformation of 4 into 6 Hydrate.

another was secured. These were carried out under the microscope and photographed. The hydrate with six molecules of water in the appropriate mother liquor was covered with a cover glass but this was not cemented to the slide. The mother liquor absorbed water from the air at the exposed edges of the glass and the $Na_2SiO_3.6H_2O$ crystals were dissolved while $Na_2SiO_3.9H_2O$ crystals formed. The change from $Na_2SiO_3.4H_2O$ to $Na_2SiO_3.6H_2O$ was similarly observed. By putting $Na_2SiO_3.9H_2O$ into a mother liquor of $Na_2SiO_3.6H_2O$, the former was slowly dissolved as the latter formed.

A series of cooling curves on mixtures 6 or 9 hydrates with water, plotting time against temperature, showed distinct changes in direction at 47° and 62.5°. At 37.2° the melting point of the probable hydrate

FIG. 25.—Sodium Metasilicate. Transformation of 6 into 9 Hydrate.
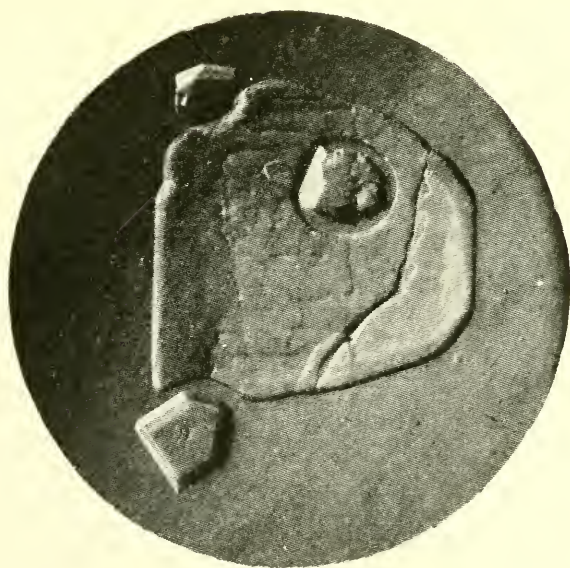
FIG. 26.—Sodium Metasilicate. Transformation of 9 into 6 Hydrate.

with 14 mols of water is indicated. The series was investigated up to 18 mols water.

Preparation of Anhydrous Metasilicate and Disilicate.

Anhydrous crystalline sodium metasilicate, Na_2SiO_3, and sodium disilicate, $Na_2Si_2O_5$, have been prepared by Morey [10] from systems at high temperatures and pressures in the presence of water. The former is formed above 400° when glass of the ratio Na_2O,SiO_2 is heated with water. The crystals are rapidly decomposed by water. The disilicate is crystallized from a glass of the same composition as the metasilicate heated at 300° with an amount of water insufficient to give complete solution. The disilicate is much less soluble than the metasilicate and can be purified by leaching with water. Long exposure to cold water causes decomposition with a residue of hydrous silica.

An investigation of the system Na_2O—SiO_2—H_2O at 25°C. was undertaken by Harman,[11] who stirred his mixtures at constant temperatures from 8 to 14 days and then analyzed the liquid and solid portions separately. This was difficult in the cases where there was little water in the system on account of great viscosity and where silica was above ratio 1:3 on account of the appearance of gel-like characteristics.

Table 26. *Analyses of Solutions and Residues.*

Solution			Residue		
Na_2O	SiO_2	H_2O	Na_2O	SiO_2	H_2O
9.37	8.74	81.89	10.51	9.94	79.55
9.45	2.22	88.33	12.48	6.75	80.77
13.70	1.19	85.11	14.50	3.46	82.04
24.48	1.34	74.18	24.02	5.48	70.50
27.52	1.84	70.64	27.25	7.52	65.23
29.58	1.90	68.51	29.74	5.04	65.22
33.02	2.92	64.06	31.96	7.57	60.47
35.54	2.94	61.52	35.70	10.06	54.24
36.39	0.49	63.12	36.75	7.75	55.50
44.78	0.85	54.37	45.31	5.82	48.87
14.11	19.65	66.25	16.20	20.26	65.54
19.32	31.33	49.35	20.18	27.71	52.11
16.57	31.30	52.23	17.72	35.44	46.84
10.53	28.80	60.67	11.19	29.95	58.86
36.75	11.65	51.60	36.07	14.90	49.03

Theoretically Calculated.

21.80	21.21	56.99	$Na_2SiO_3.9H_2O$		
26.93	26.18	46.89	$Na_2SiO_3.6H_2O$		
37.06	36.04	26.89	$Na_2SiO_3.2.5H_2O$		
50.69	49.31	....	Na_2SiO_3		
17.99	34.98	47.00	$Na_2O.2SiO_2.9H_2O$		
53.45	....	46.55	$NaOH.1H_2O$		

[10] Morey, G. W., *J. Am. Chem. Soc.*, **36**, 215 (1914).
[11] *J. Phys. Chem.*, **31**, 511-518 (1927).

He confirmed the existence of $Na_2SiO_3.6H_2O$ and $Na_2SiO_3.9H_2O$—the hexa- and ennehydrates of sodium metasilicate and concluded that the only other hydrate stable at 25°C. contains 2.5 molecules of water; and he plotted the areas in which they constitute the stable phase. As a hydrate with 2.5 molecules of water has not been isolated and as Erdenbrecher appears to give conclusive evidence of a definite hydrate
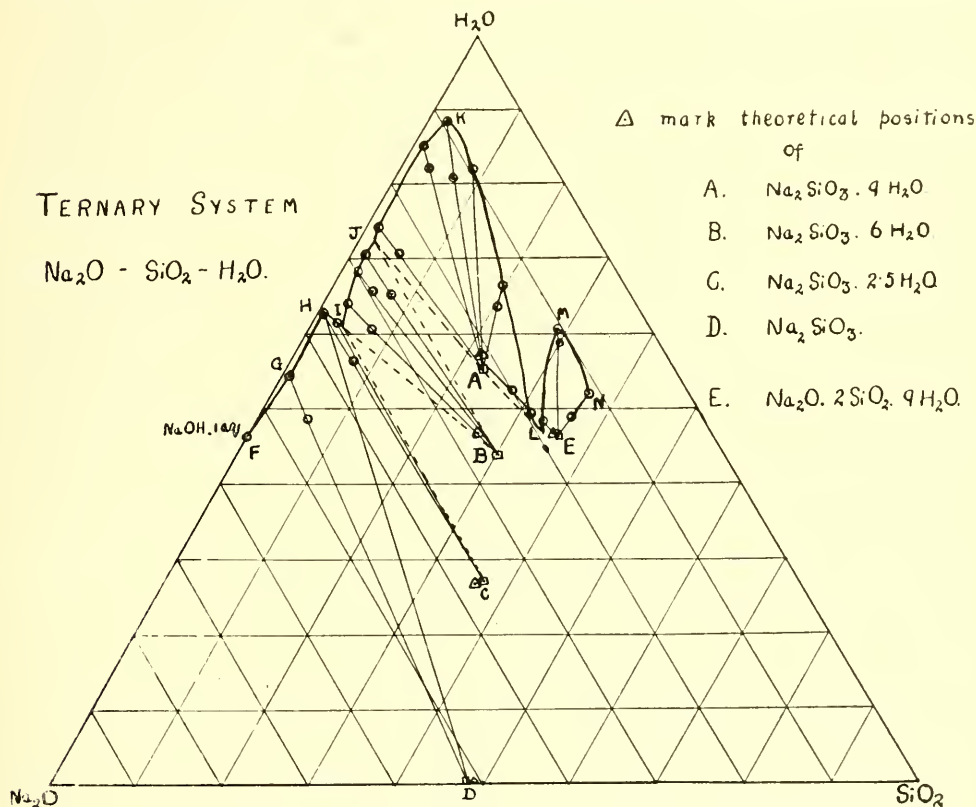
FIG. 27.—Ternary System. $Na_2O = SiO_2 = H_2O$.

with less water than $Na_2SiO_3.6H_2O$, which he believed to be $Na_2SiO_3.4H_2O$, the conclusion that only the three hydrates can exist at 25° must be received with reservations.

An area was found, before experimental difficulties concluded the study, in which the disilicate $Na_2O,2SiO_2.9H_2O$ was indicated. This has never been isolated at ordinary temperatures though there are many evidences of its existence.

ANHYDROUS SYSTEMS.

Sodium metasilicate, Na_2SiO_3, and sodium disilicate, $Na_2Si_2O_5$, have been crystallized from anhydrous fusions by Niggli [12] and Morey.[13]

[12] Niggli, Paul, *Z. anorg. Chem.*, **84**, 229-272 (1913).
[13] Morey, G. W., *J. Am. Chem. Soc.*, **36**, No. 2, 215 (1914).

Schwarz and Menner [13a] claim to have produced another definite crystalline compound, $Na_2O.3SiO_2$ from a glass of that composition, which on long heating became crystalline. Their evidence is inconclusive. Morey and Bowen [14] found that the optical properties of metasilicate and disilicate were very nearly alike, differences being shown only by very exact measurement of their optical constants. They both have positive elongation and low refractive indices, and are apparently orthorhombic. Table 27. The melting point of the metasilicate is in close agreement with that found by Jaeger.[15]

$$Na_2SiO_3—1088°, \text{ Jaeger}$$
$$1086°, \text{ Morey}$$
$$Na_2Si_2O_5—874°, \text{ Jaeger and Morey}$$
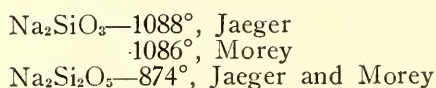
TABLE 27. *Optical Constants of Sodium Metasilicate and Sodium Disilicate.*
(Morey and Bowen)

	Na_2SiO_3	$Na_2Si_2O_5$
Crystallization	Orthorhombic	Orthorhombic
Habit	Needles	Plates and needles
Cleavage	Prismatic in zone of γ	Pinacoidal
		$\gamma\beta$ and $\gamma\alpha$
Optic axial angle............	2V very large	2V = 50° to 55°
Optical Character	Negative	Negative
Refractive indices .... γ	$1.528 \pm .002$	$1.518 \pm .002$
β	$1.520 \pm .002$	$1.514 \pm .002$
α	$1.513 \pm .002$	$1.504 \pm .002$

POTASSIUM SILICATES.

Morey and Fenner also determined the melting points of K_2SiO_3 and $K_2Si_2O_5$. Potassium silicates, owing to their great deliquescence, were not prepared in crystalline form until Morey,[16] in an investigation designed to throw light on the equilibria existing in rock magma, studied the system K_2SiO_3—SiO_2—H_2O at temperatures from 200° to 1000° C. Glasses of known composition were made by fusing potassium carbonate or potassium hydroxide with silica. These were heated with silica and water in a bomb so made that no vapor could escape. The desired temperature was maintained in an electric resistance furnace until equilibrium was established and then by cooling rapidly a series of hydrous solids was produced which showed the equilibrium which

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[13a] Schwarz and Menner, *Ber.*, **57B**, 1477-1481 (1924).
[14] Morey, G. W., and N. L. Bowen, *J. Phys. Chem.*, **28**, No. 11, 1167-1179 (1924); *Ber.*, **57B**, 1477 (1924); **58B**, 73 (1925).
[15] Jaeger, F. M., *J. Wash. Acad. Sci.*, **1**, 49-52 (1911); Abst. in *J. Chem. Soc.*, **100A**, 2981-2982; *C. A.*, **5**, 3770.
[16] Morey, G. W., *J. Am. Chem. Soc.*, **39**, 1173-1229 (1917). Cf. Pukall, W., *Ber.*, **49**, 397-436 (1916).

had existed at the higher temperature. Microscopical examination of the quenched products made it possible to fix the amounts of the glasses of each composition which would remain dissolved at the temperature in question. The crystalline products were identified by means of their optical constants and their composition fixed by study of the isothermal saturation curves and checked where possible by the analysis
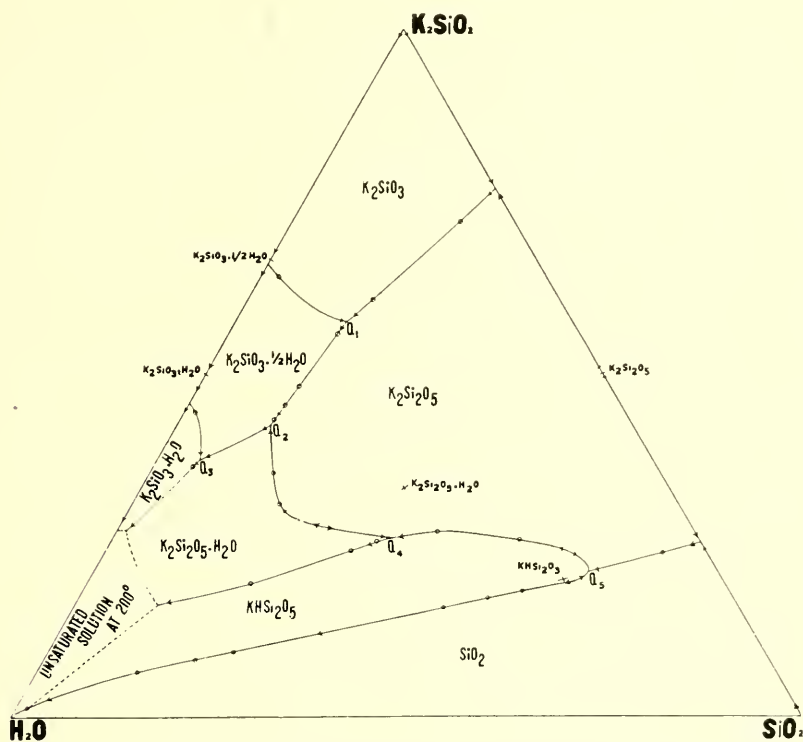
FIG. 28.—The System Potassium Metasilicate, Silica, Water. Diagram showing the boundary curves. The compound stable in contact with liquid in each field is shown by the large letters; the point representing the composition of the compound, by the small letters. Arrows show the direction of falling temperature. The broken line is the isotherm at 200°.

of pure compounds or by the method of residues. Six potassium silicates were thus identified.

$KHSi_2O_5$—decomposed by H_2O below 420°. As observed under the microscope the action is so slow that it appears to be practically unattacked by H_2O.

$K_2Si_2O_5$—melts at 1041° and is not decomposed by H_2O. The crystals break up irregularly in water under the microscope showing characteristic shred-like forms as they go into solution.

$K_2Si_2O_5.H_2O$—rapidly decomposed by water at ordinary temperatures. Crystals dissolve completely.

K_2SiO_3—melts at about 966°. It is very hygroscopic and crystals dissolve rapidly and uniformly.

$K_2SiO_3.\frac{1}{2}H_2O$—completely soluble in water.

$K_2SiO_3.H_2O$—decomposed by H_2O at temperatures below 200°. It breaks down at 370° into $K_2SiO_3.\frac{1}{2}H_2O$ and vapor. Crystals dissolve completely in water.

LITHIUM SILICATES.

Solutions of lithium silicate have been studied by Ordway[17] but he did not succeed in isolating any definite compounds. He precipitated sodium silicate solutions with solutions of lithium chloride and obtained a cake composed of a mixture of sodium and lithium silicates. This was dissolved in water and the process repeated with increase of Li_2O in the cake. Finally a solution was obtained containing $2(Li_2O,4SiO_2)$, $Na_2O,4SiO_2$. A solution containing 8.5 per cent Li_2SiO_3 and a slight excess of LiOH was prepared by the action of LiOH on hydrous silica. This could not be concentrated above 11 per cent.[18] Four definite lithium silicates have been prepared by fusion but none of them dissolves without decomposition. A difficultly soluble lithium metasilicate monohydrate is described by Vesterberg[19] as precipitated by heating to 80° solutions made from hydrous silica and twice the theoretical amount of $2 N$ LiOH at ordinary temperatures. Solutions containing 3.4 mols SiO_2 for each Li_2O were made with $2 N$ LiOH and hydrous silica. Carter[20] in attempting to prepare solutions of lithium metasilicate, found that a clear glass of the composition Li_2O, $2SiO_2$ could be prepared from the carbonate by fusion with silica at 1300° and dissolved with some decomposition to a solution containing 6 per cent Li_2O, $3.2SiO_2$ but not entirely free from carbonate. The melts corresponding to the metasilicate cooled to crystalline masses which decomposed with the separation of hydrous silica but could not be brought into solution. The system Li_2SiO_3–SiO_2 was worked out by Jaeger and van Klooster.

RUBIDIUM SILICATES.

Rubidium metasilicate does not crystallize under ordinary conditions.[21] A solution of rubidium hydroxide containing 21 per cent Rb_2O readily

[17] Ordway, J. M., *Am. J. Sci.*, 174, 4th Ser., 473-478 (1907).

[18] Le Chatelier, "La Silice et les Silicates," 1914, p. 400-401; Jaeger and H. S. van Klooster, *Proc. Acad. Sci. Amsterdam*, 16, 857-880 (1914).

[19] Vesterberg, K. A., *Medd. K. Velenskapakod, Nobel Inst.*, 5, No. 30, 1-9 (1919).

[20] From the unpublished records of the Philadelphia Quartz Company (1917).

[21] Ordway, *loc. cit.*

dissolved enough silica in hydrous condition to give Rb_2SiO_3 but yielded a thick viscous liquid at 83 per cent solid content. This when diluted took up enough silica to form disilicate, but no crystallization took place. Precipitation by alcohol gave compounds of higher SiO_2 content up to $Rb_2O, 4SiO_2$, which was freely soluble in water.

Chapter IV.

Reactions.

Compounds Causing Precipitation.

So many substances react with and precipitate silicate solutions that it is almost safe to assume that a clear viscous solution of any alkaline silicate contains nothing but silica, alkalies, and water. At least from the point of view of the analyst, it is possible to eliminate so many classes of compounds that examination is relatively simple. Yet, because the commercial solutions are viscous and partake of the nature of colloids, it is possible for trifling quantities of the most various substances to be present.

Mineral Acids and Acid Salts. The substances which may be mixed with silicate solutions without reaction are few in comparison with those which react. All strong mineral acids are able to bind alkali metal and liberate silica which remains as a sol or separates in gel form according to the amount of water or electrolytes present and to the temperature, time, and other factors. Even carbon dioxide and hydrogen sulfide are absorbed when conducted into silicate solutions, and when the concentration is sufficient may cause precipitation. Acid salts, such as bicarbonates, bichromates, and bisulfates of the alkali metals, produce similar results.[1]

Other Salts and the Halogens. All soluble compounds of metals which form insoluble silicates, i.e., all except the alkali metals, also react with silicate solutions. In this category are included the zincates, aluminates, and plumbates of the alkali metals but not their chromates or permanganates. Fluorine, chlorine, and bromine react but iodine is much less active. Ammonium salts in concentrated solution will precipitate soluble silicates with the liberation of ammonia. This reaction is used to render silicate of soda insoluble **as a binder for decorative** colors on glass. Cold ammonium hydroxide, sp. gr. 0.921, will precipitate $Na_2O,3SiO_2$ at sp. gr. 1.392.[2]

[1] Basset, L. P., Fr. Pat. 410,038 (March 4, 1909).
[2] Fluckiger, F. A., *Buchner's neues Repertorium für Pharmacie,* **19,** 260 (1870) ; *American Chemist,* **2,** 64 (1871).

Certain Organic Compounds. Commercial sugar, dextrin, glucose, glycerin, and gum arabic (after it is freed from naturally occurring soluble salts) are miscible with silicate of soda solutions of commerce. Phenol, chloral hydrate, tannic acid and most organic compounds which readily react with alkalies cause precipitation with concentrated silicates.

Alcohols. Ethanol and methanol produce precipitates from concentrated silicate solutions. These are mostly soluble in water and are to be regarded as dehydration products. Von Fuchs[3] proposed this reaction as a distinction between silicates of soda and potash, as the latter is more difficult to precipitate, but since both may be precipitated from strong solutions the test has very little value.

PRESENCE OF PRODUCTS OF HYDROLYSIS.

Few of these reactions have been carefully investigated; but it is safe to make the general statement that, as we are dealing with colloidal material, the character of the products of reaction will vary in every case with changing conditions. The assumption that even definite silicates such as sodium metasilicate will react quantitatively with metallic salts of definite composition in solution to form definite insoluble silicates will lead to serious error. Attempts to prepare metallic silicates in the wet way would never be expected to lead to simple, definite products but always to a mixture in which one or more silicates are associated to a greater or less degree with hydroxides, complex silicates, and silica.[4]

The simple equation:

$$Me''X_2 + Me'SiO_3 = Me''SiO_3 + 2Me'X$$
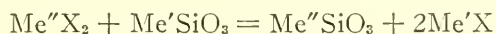
never represents the observations of experimental work. The products of reaction are not the simple ones which might be expected if hydrolysis were complete and the metallic salts should cause the separation of the corresponding hydroxide and silicic acid. Equilibrium is attained but slowly, changes in some cases taking place over a period of years.

It does not follow that because the bases are present in equivalent amounts a neutral product will be obtained or that because the reaction product is an insoluble substance it will not remain dispersed as a sol in the aqueous reaction medium or that the phenomena observed at one temperature can be forecast from those at another.

[3] *Dingler's polytech. J.,* **142**, 365-392 (1857).
[4] Jordis and Hennis, *J. prakt. Chem.,* **77**, 226 (1908).

REACTIONS OF METALLIC SALTS.

This being so, it follows that experimental work, to be of value, must be carried out under the most precise control of all variables which have an influence. Jordis and his collaborators have followed a few of these reactions with great thoroughness and care. In the effort to use only solutions of known composition, sodium metasilicate was selected, and its reactions with solutions of cupric sulfate, ferrous sulfate, and ferric chloride investigated.[5]

Copper. The metasilicate of copper occurs in nature with one and two molecules of water in definite crystal form as dioptase and chrysocolla respectively. The former was prepared by Becquerel,[6] who placed cupric nitrate and potassium silicate on opposite sides of a permeable membrane. The diffusion which brought the two solutions together was slow, permitting the formation of crystals but at the same time holding back colloidal constituents of the solutions which would have interfered with the definite character of the result.

Jordis and Hennis [7] mixed 0.1 molar solutions of sodium metasilicate and copper sulfate in equal amounts quickly and with agitation under varying conditions.

	Total Per Cent of Silica Found in Filtrate
Copper solution poured into silicate..................	3.53
Silicate poured into copper solution..................	4.75
At boiling temperature.............................	4.03

When the amount of silicate solution was doubled the filtrate contained 43.8 per cent of the total silica. The first three experiments show that the reaction is not a simple exchange of molecular equivalents as silica remained in solution while all the copper was precipitated, and further evidence of complicated relations lies in the fact that when the amount of silicate was doubled the additional silica thus

TABLE 28. *Results of Precipitation.*

Mols CuO per Mol SiO_2	Per Cent of the Original Silica in the Filtrate
3	31.87
2.24	14.40 (33.1 CuO %)
1.12	1.24
1.00	3.88
0.56	26.37
0.50	41.91 av. $\begin{cases} 43.83 \\ 40.00 \end{cases}$

[5] Hennis, W., Dissertation, Erlangen, **1906.**
[6] *Jahresber. der Chem.* (1868), 87-90; *Compt. rend.,* **67,** 1081 (1868).
[7] Jordis and Hennis, *J. prakt. Chem.,* **185,** 238-266 (1908).

introduced did not all appear in the filtrate, which showed but 43.8 per cent compared with an expected 54 per cent.

Equal measures of N CuSO$_4$ and N silicate of soda of composition Na$_2$O,2SiO$_2$, gave 4.47 per cent of the total silica in the filtrate. When the ratio of volumes was 1 : 0.983, the silica was reduced to 3.24 per cent. The precipitates, at first amorphous, developed microscopic green crystals on standing. Evidence of the presence of a copper silicate in the precipitate rather than a mixture of copper hydroxide and silica was the color of the precipitates on boiling. Copper hydroxide becomes black on boiling but the precipitates of blue copper silicate under like treatment did not go beyond a green. The color is not changed to black if mixtures of gelatinous silica and copper hydroxide are rubbed together and then boiled.

Iron. Ferrous silicates in various minerals and slags are blue green to green in color and relatively stable. Precipitated ferrous silicate mixtures are, however, very easily oxidized to a yellow color in acid solutions and become grayish in alkaline solutions. The stability of the minerals containing ferrous iron may be in part accounted for by the presence of basic constituents.

Tenth-molar solutions of ferrous salts with equal volume of 0.1 molar sodium metasilicate gave iron-free filtrates containing an average of 1.8 per cent of the silica, and excess of either constituent, as in the case of copper, increased the silica in the solution. The silicate precipitates did not become black like ferrous hydroxide on boiling in the mother liquor. Tenth-molar ferric chloride which was made acid with hydrochloric acid and neutralized with sodium hydroxide, then mixed with equivalent 0.1 molar sodium metasilicate, gave a variety of precipitates under varying conditions of heating, mixing, and standing. All the filtrates had an acid reaction. A few typical analyses of unwashed ferric precipitates are given in the table below.

TABLE 29. *Composition of Precipitates (Unwashed).*

SiO$_2$	Fe$_2$O$_3$	Na$_2$O	Cl	H$_2$O
39.35	45.48	2.80	1.3	11.37
33.45	42.95	4.68	...	19.03
29.91	41.36	3.57	...	25.29
26.39	18.53	15.74	10.37	(33.51)

It is obvious that no definite substance, but a mixture, is thrown out of these solutions. If methyl orange or phenolphthalein be added to the silicate solution during the precipitation of a gelatinous precipitate the color is largely carried out of the solution with the precipitate and shows the alkaline color in spite of the presence of an acid

supernatant liquor. Adsorption of sodium ions on the silicious precipi-
tate probably accounts for this. Large additional amounts of caustic
alkali must be added to bring about an alkaline reaction whether or
not the clear solution and the precipitate are separated by filtration.
On standing, the alkalinity vanishes and only after several additions
does the solution remain alkaline. If all the alkali is added at once,
a smaller amount is required to neutralize than when it is added a little
at a time or slowly.[8] After the ferric chloride solutions had been
carefully adjusted to the composition $FeCl_3$ and a similarly standard-
ized sodium metasilicate was used and filtered promptly the clear
filtrate contained all the ions of the original solutions but none of
them in stoichiometric relations. If the clear filtrate is boiled precipi-
tation occurs. The addition of an electrolyte, such as Na_2SO_4, will
also cause precipitation. If the original precipitate and supernatant
liquor are allowed to remain long in contact both are changed and
eventually the acidity will disappear.

2Na : $1SiO_2$ and 0.66Fe : 2Cl were mixed. No precipitate formed
at first but in about 7 minutes it began to separate as a gelatinous pre-
cipitate and the filtrate showed the analysis given below, after the time
stated.

TABLE 30. *Progress of Precipitation (Mols).*

	Na	SiO_2	Fe	Cl
After 13 min.	2.55	1	3.86	0.95
23 min.	8.08	1	.78	7.70
83 min.	10.80	1	.23	9.43
5 hrs.	13	1	.54	12.50
24 hrs.	19.15	1	.50	19.50
5 days	21.2	1	.60	23.50

At first, silica is precipitated with much chlorine and goes into so-
lution. As time goes on, silica and iron are further precipitated and
sodium and chlorine approach molecular relations.

The character of precipitation when ferric chloride solution is
added to silicate solution is different from that yielded by the reverse
procedure. An excess of either component reduces the amount of pre-
cipitation when the two solutions are poured quickly together. When
iron solution is added in small portions to silicate solutions precipita-
tion occurs at once but half of the silicate solution can be added to the
iron solution without causing turbidity. The liquid only becomes pro-
gressively darker.

Experiments made with a 40° Baumé commercial silicate of soda solu-
tion (probably about $Na_2O,3SiO_2$) and ferric chloride led Liesegang [9]

[8] Jordis and Lincke, *Z. angew. Chem.,* **21**, 11, 1982-1986 (1908).
[9] *J. prakt. Chem.,* **88**, 358 (1913).

to the belief that only ferric hydroxide and hydrous silica were precipitated and the attempt to work with pure compounds had led to more complicated phenomena. A solution of ferric chloride flowed over the viscous silicate increased in volume and gradually formed a gelatinous film even between the glass and the silicate, finally completely enveloping the latter. This translucent film was streaked with ferric hydroxide, which could be partly removed by a jet of water and almost completely with dilute acid. A similar firm silicious membrane was formed when 15 per cent hydrochloric acid was poured over the 40° silicate, the acid diffusing into the silicate solution, although acid of 2 per cent strength yielded a soft gelatinous mass. An interesting variation of the film or membrane that forms when concentrated colloidal silicates come in contact with relatively strong solutions of ferric chloride or other metallic salts is known as the "silicate garden." * Crystals of ferric chloride dropped into a viscous silicate solution will be promptly surrounded by a membrane through which an aqueous liquid diffuses under osmotic pressure.

Aluminum. The reactions between sodium metasilicate and aluminum sulfate and chloride were studied by Gottwald.[10] The compositions of the solutions were precisely adjusted to correspond with the formulas but the flocculent precipitates always contained sodium along with aluminum silicate. Both silica and aluminum compounds remained in the filtrate, although the amount of aluminum was very small after standing. The reaction did not cause noticeable temperature changes. The precipitate was first weakly acid to litmus and then neutral. When precipitates were formed in the presence of Cl ions, they were more easily separated by filtration or by settling than in the presence of SO_4 ions.

Sodium in the filtrates was nearly equivalent to the anion but in relation to the silica it was much greater in the chloride series than when the aluminum was present as sulfate. The average molecular relations in the precipitates are shown in the following tables:

TABLE 31. *Precipitates from Equivalent Amounts of Sodium Metasilicate and Aluminum Sulfate.*

(Concentrations between 1 and 2 per cent.)

Time	Mols SiO_2	Mols Al	Mols SO_4	Mols Na
1 hr.	1.0	0.8720	0.0469	.....
1 " 25 min.	1.0	0.7633	0.0358	0.1899
4 "	1.0	0.7205	0.0124	0.3695
8 days	1.0	0.6786	0.0665	0.2770
14 "	1.0	0.6421	0.0940	0.4120

* Cf. pages 79-80.
[10] Gottwald, Dissertation, Erlangen, **1913**; *Neues Jahrbuch Min. Geol.,* **11**, 51-53 (1915).

TABLE 32. *Sodium Metasilicate and Aluminum Chloride.*

Time	Mols SiO₂	Mols Al	Mols SO₄	Mols Na
45 min.	1.0	0.9341	0.1078	0.1352
48 "	1.0	0.8328	0.0927	0.2015
3 hr. 45 min...........	1.0	0.9849	0.0764	0.1359
1 day	1.0	0.9072	0.0650	0.1376
8 days	1.0	0.7526	0.0627	0.1210
10 "	1.0	0.6735	0.1179	0.1753
14 "	1.0	0.7280	0.0733	0.1195
4 months	1.0	0.6813	0.0656	0.1954

An attempt to determine whether aluminous precipitates from high ratio silicates contain free silica was made by Carter,[11] who found them
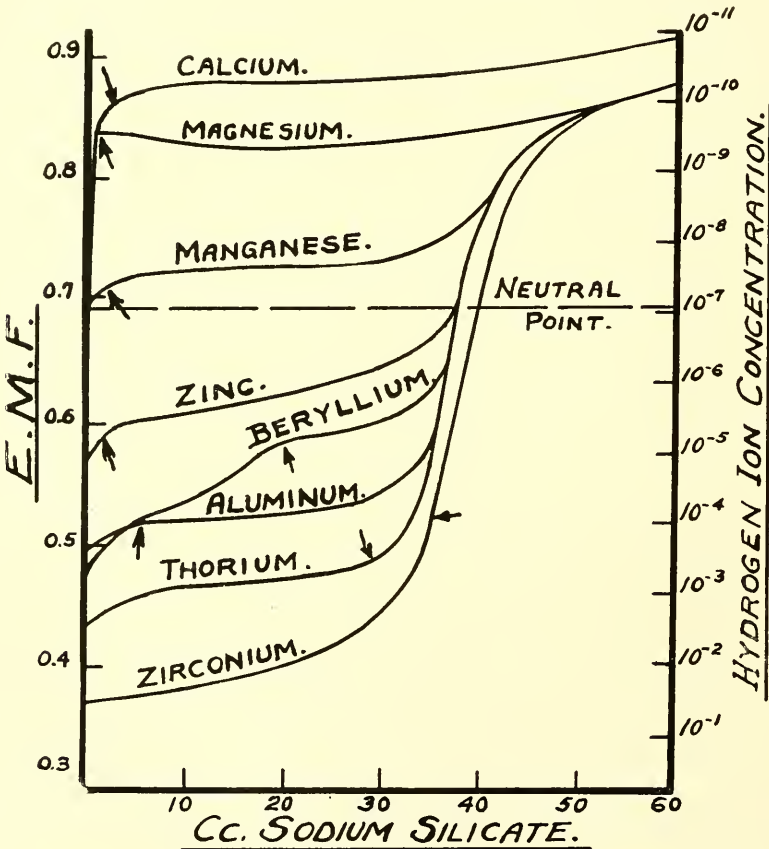
FIG. 29.—Electrometric Study of Precipitation of Silicate Solution Na₂O, 2.16SiO₂ with Metallic Salts (Britton).

completely soluble in a hot solution of sodium hydrogen sulfate which did not dissolve a freshly made precipitate of silica.

Electrometric titrations of a solution of $Na_2O, 2.16SiO_2$ with hydrochloric acid, alkaline earth hydroxides and various metallic salts have

[11] Unpublished records of Philadelphia Quartz Company.

been made by Britton.[12] When all the alkaline earth metals had been precipitated more silica was found in the precipitate than that which had been held by an amount of sodium equivalent to the alkaline earth metal. The conditions of his experiments were as follows: Na_2O, $2.16SiO_2$ in a solution 0.102 normal with respect to its sodium content was used for hydrogen electrode titrations of 100 cc. portions of salt solutions of the strengths indicated in the following table. The temperature was 18°C. and the time at which a precipitate first appeared was noted. The pH values of the silicate precipitations were compared with the known data for hydroxide precipitation.

TABLE 33. *Electrometric Titrations with a Solution of $Na_2, 2.16SiO_2$.*

Solution Titrated	Precipitation Began at		Hydroxide Precipitation at pH
	pH	cc. of Sodium Silicate	
0.01 M — ZrCl₄	3.98	35.0	1.86
0.01 M — ThCl₄	3.50	30.0	3.50
0.0067 M — Al₂(SO₄)₃	4.04	5.0	4.14
0.02 M — BeSO₄	5.31	20.0	5.69
0.02 M — ZnSO₄	5.25	1.0	5.20
0.02 M — MnCl₂	7.35	1.0	8.41
0.02 M — MgSO₄	9.50	1.0	10.49
0.02 M — CaCl₂	10.07	3.0	....

In this connection see also the work of Oka and Noda,[13] Joseph and Oakley,[14] and Hägg.[15]

SILICATE GARDEN

The familiar experiment known as the "silicate garden"[16] is an example of reaction at a higher concentration. The substances which appear as flocculent precipitates when much water is present have a firm texture when strong solutions react. Crystals of easily soluble salts of the heavy metals when dropped into suitable silicate solutions begin to dissolve, and reacting, are soon encased in a film of gel-like character. Water from the silicate solution diffuses through the permeable membrane to dissolve more of the salt. The osmotic pressure soon becomes sufficient to deform or burst the cell wall. Thus new surfaces of salt solution are exposed which continue the process and form long tendrils or fungoid growths. The speed with which this curious reaction takes place varies with the concentration and rela-

[12] *J. Chem. Soc.*, **127**, 2814 (1925).
[13] Oka and Noda, *J. Sci. Agri. Soc.* (Japan), **258**, 287 (1924).
[14] Joseph and Oakley, *J. Chem. Soc.*, **127**, 2814 (1925).
[15] Hägg, *Z. anorg. Chem.*, **155**, 20 (1926).
[16] Krug, George C., U. S. Pat. 1,584,779 (May 18, 1926).

tive alkalinity of the silicate, being more rapid and yielding more fragile formations in dilute solutions and developing more rapidly in solutions of higher alkalinity when the concentration is the same. Many soluble salts yield growths of more or less characteristic form.
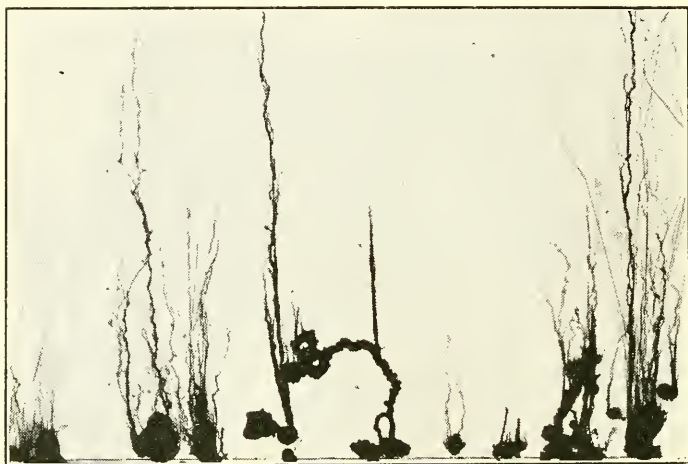
Fig. 30.—Silicate Garden.

The layer with which the crystal is surrounded is at first liquid, but the sol goes over into the rigid gel condition in a longer or shorter time, according to circumstances. Quincke [17] worked with solutions of the composition $2Na_2O,3SiO_2$ and found the setting time to be as follows:

```
0.3 to 0.5 second   with FeCl₃ and NiCl₃
15 to 20  seconds with MnCl₂
1   to 30  seconds with CuSO₄
120        seconds with CuCl₂
```

The gel formed at the interface between silicate and hydrochloric acid may, under favorable circumstances, remain liquid for months. During the liquid phase, bubbles are formed due to surface tension. These solidify before equilibrium is established and as the liquid penetrates under osmotic pressure, the shape of the walls is distorted in curves or broken according to their texture at the moment. This gives rise to the most various forms. The cell walls or tubular filaments give up water (syneresis) on solidifying and become opaque so that a varicolored garden such as can be made from copper, nickel, cobalt, iron, manganese, and uranium salts, increases in beauty for some days after the filaments have ceased to grow. One of the best ways to exhibit this reaction is to make a cell of glass about four inches square and place in it layers of silicate solution of varying concentration, thus

[17] Quincke, G., *Ann. Physik.*, **312**, ser. 4, v. 7, 631.82 (1902).

changing the growths as they pass from one level to another. Silicates of the composition $Na_2O,2SiO_2$ at specific gravities 1.090, 1.045, and 1.015, are a convenient series. The diffusion of the silicates is so slow that if carefully prepared, they will remain in separate layers for a long time.

A good example of the importance of describing the chemical composition of any silicate used in experimental work is afforded by the work of Ross,[18] who reported that uranium nitrate and acetate would not grow in a silicate solution of the sort used for preserving eggs. This is very indefinite but from the relatively meager growths secured, it seems likely that the composition approached $Na_2O,4SiO_2$. Uranium salts will produce fungoid forms of brilliant yellow color and great beauty in a silicate of the composition $Na_2O,2SiO_2$.[19]

Fractional Precipitation by Alcohol.

Fractional precipitation of silicate solutions with ethanol, methanol, or acetone, was found by Ordway [20] to be a useful means of eliminating, at least partially, other compounds which might be present. A 10 per cent silicate of soda solution is mixed with a tenth its volume of 95 per cent alcohol and the precipitate rejected. Two volumes of alcohol added to the filtrate cause a voluminous white opaque precipitate which, when well drained, contains about 50 per cent water. A mass of this precipitate allowed to stand will flatten out and become increasingly translucent. The first precipitation carries down most of the alumina. lime, magnesia, or heavy metal compounds which may have been in the original silicate, but iron cannot be entirely removed in this way. The alcoholic supernatant liquor contains most of the sodium chloride or sulfate from the silicate solution. The precipitate can be dissolved in four parts of water and the operation repeated. Ignition of silicates precipitated from alcohol, even after they appear quite dry, is accompanied with a blackening not only indicative of the incomplete removal of organic matter but suggesting that there may be a reaction between the silicate and alcohol. This has not been investigated.

Alcoholic precipitates of silicates of soda more alkaline than Na_2O, $1.7SiO_2$ are generally liquid but as the relative amount of silica increases, the masses are progressively firmer, though even the hardest retain the ability to flow slowly at ordinary temperatures. This is

[18] *Proc. Roy. Soc. N. S. Wales*, **44**, 583-592 (1910).
[19] Dollfus, Robert, *Compt. rend.*, **143**, 1148-1149 (1906).
[20] *Am. J. Sci.*, **83**, ser. 11, v. 33, 27-36 (1862).

characteristic of all silicate solutions which, like those precipitated by alcohol, contain about 50 per cent of water.

The more dilute the silicate solution in which a precipitation is induced by alcohol, the greater will be the difference between the composition of the separated material and the original solution. The more water present, the greater will be the Na_2O in the supernatant liquid and correspondingly the more silicious the precipitate. Ordway obtained precipitates as silicious as $Na_2O, 4.78SiO_2$, but his statement that they were insoluble must not be taken as final because he boiled them with an excess of water and we now know that the favorable condition for bringing such materials into solution is to treat them first with very little water or even to allow them to absorb water from an atmosphere of steam.

Ammonia.

Ammonia yields soluble precipitates from silicate of soda solutions. As with alcohol, the precipitate tends to have a higher silica ratio than the solution and this tendency increases with increasing water. The following examples are from Ordway.[21] Forty cc. of ammonium hydroxide of specific gravity 0.900 mixed with 50 grams of a 29 per cent solution of $Na_2O, 3.66SiO_2$ yielded a precipitate containing 43 per cent of $Na_2O, 3.4SiO_2$. The same amount of ammonia added to 50 grams of a 21 per cent solution of $Na_2O, 3.8SiO_2$, gave a ratio of $Na_2O, 4SiO_2$ in the precipitate.

Gelation.

Any reaction for the precipitation of a soluble silicate can be made to yield a gel provided it is possible to mix thoroughly the reacting substances at an appropriate concentration before a separation takes place. The gel, including the whole solution, may form in neutral, strongly acid, or strongly alkaline solutions and at concentrations from one to twenty-five per cent or perhaps even higher. The density of the gel even after it has been slowly dried and completely dehydrated will depend on the density of the original solution in which it formed. The porosity of the gel structure appears to be related also to the time consumed in passing from the sol to the gel condition.

Crystals and Rhythmic Banding.

Not only acids and alkalies, but many salts, may be present during the process of silica or silicate gel formation and as the gel is easily

[21] *Am. J. Sci.*, **24**, ser. 4, 473-478 (1907).

permeable it offers a convenient means for bringing two reacting solutions together so gradually that crystals are formed of much greater size and beauty than result from mixing the solutions directly. Thus, Holmes[22] prepared lead iodide, metallic gold, etc., and Liesegang [23] produced examples of rhythmic banding very like the patterns which are so familiar in agates.

RELATION BETWEEN COLLOIDAL SILICATES AND CELL STRUCTURE.

Metastable dilute silicate solutions have been shown to yield cell-like structures closely suggestive of the forms of animate organisms. Thus Moore and Evans [24] following the suggestions of Bastian,[25] who reported spontaneous growth of living cells, were able to produce growths of diverse form in solutions from which all organic matter had been excluded with extreme precautions. Silicate of soda of specific gravity 1.44 (presumably $Na_2O,3SiO_2$) was used and solutions prepared with ferric nitrate. In one case, 10 cc. of a 1 per cent solution of ferric nitrate was treated with 4 cc. of a 1 per cent solution of the silicate and shaken well, and after standing, a membranous precipitate formed. One to two per cent sols, stable for 3 weeks, yielded micro-structures of fibrous character.

In another case a solution containing 0.03 per cent ferric nitrate and about 0.2 per cent silicate, which was clear yellow and yielded a slight deposit on boiling for ten minutes, produced a variety of microscopic plant-like growths when left in sealed tubes for several weeks. Additions of ammonium phosphate and sodium carbonate varied the forms somewhat, but did not bring them nearer to the character of living organisms.[26]

Herrera [27] carried the study further and concluded that colloidal silicates yield structures most like natural forms when produced from reaction-mixtures of very low concentration, when contact between precipitating agents is made slowly and when the viscosity of the reacting solutions is great.

The problem of the spontaneous generation of life is a fascinating field of research and quite unsolved, though it must be remarked that the many repetitions of his experiments by Bastian, and the care with

[22] Holmes, H. N., *J. Am. Chem. Soc.,* **40,** 1187-1195 (1918).
[23] Liesegang, Raphael Ed., *Z. anorg. Chem.,* **48,** 364 (1906) ; *Z. physik. Chem.,* **59,** 444 (1907).
[24] Moore and Evans, *Proc. Roy. Soc. (London),* ser. B. **89,** 17-27 (1915).
[25] Bastian, *Nature,* **92,** 579 (1914) ; *Proc. Roy. Soc. Med.,* **8,** 55-68 (1915).
[26] Onslow, H., *Nature,* **98,** 489-490 (1917) ; *Proc. Roy. Soc. (London),* **90B,** 266-269 (1918).
[27] *J. Lab. Clin. Med.,* **4,** 479-483 (1919).

which they were executed, point strongly toward the view that the cells which started the long chain of evolution were probably produced in silicate solutions comparable to those with which Bastian worked.

ELECTROLYTES.

The action of electrolytes which are not decomposed by the silicate solutions presents a series of interesting phenomena. Fluckiger [28] records that when equal parts of a certain silicate of soda of 1.392 specific gravity and a solution of sodium nitrate in twice its weight of water were mixed there was no precipitation, but that on heating to 54° he obtained an almost complete gel which redissolved on cooling. Larger

FIG. 31.

amounts of sodium nitrate retarded and finally prevented this redissolving. He also notes that potassium bromide is miscible in the cold but causes precipitation on heating. Saturated solutions of sodium sulfate added to concentrated silicious sodium silicates cause precipitates which dissolve on dilution.

Malcolmson [29] and Stericker [30] have studied the action of sodium chloride solutions when mixed with relatively concentrated silicates of soda. It was first found that by the use of brines of appropriate strength, the volume of adhesive silicate of soda solutions could be extended more than 20 per cent without reducing the viscosity. A 16 per cent brine will cause a gelatinous precipitate in a concentrated silicate solution of composition $Na_2O, 3.5SiO_2$, but this may be dis-

[28] *Chem. Zentr.,* **41**, ser. B 1, 639 (1870).
[29] Malcolmson, J. D., *Ind. Eng. Chem.,* **12**, 174 (1920).
[30] Stericker, unpublished report of Mellon Institute of Ind. Research.

persed by stirring, after which the solution is thicker than before and remains so permanently. Mylius [31] found that sodium chloride would not precipitate silica from solutions less alkaline than $Na_2O,2SiO_2$, but an effort to relate the amount of sodium chloride required to restore the viscosity of the more silicious silicates to their silica content did not succeed. It was found that the addition of brine changed the hydrogen-ion concentration of the silicate which passed through a minimum when the original viscosity was restored. The formation of adsorption compounds may account for this. Dehydration may have a part in this phenomenon but does not account for all the variations in pH value.

Other electrolytes may be manipulated to bring about similar changes but they have not been studied.

REACTION WITH COLORING MATERIALS.

Many dyestuffs which are soluble in alkaline solutions are so completely salted out of strong silicate solutions as to be useless for coloring them. A few of the most soluble are available, among them, rhodamine, fluorescein, and various eosin colors. Alkaline tannates are effective coloring agents for silicate solutions. Any silicate of soda solution sufficiently dilute to be fluid will draw a rich coffee brown color from a red oak barrel and such extracts as cutch, made strongly alkaline with sodium hydroxide, serve the same purpose. A good blue may be made by adding glycerin to a copper salt and making it strongly alkaline with caustic soda before adding to the silicate. Yellow solutions are best made with chromates.

REACTION WITH VARIOUS SOLID COMPOUNDS.

There remain to be mentioned the reactions which take place between silicate solutions and various solid substances which have a technical importance in the manufacture of various cements, which will receive separate consideration in a later chapter.

Dilute hot solutions of $Na_2O,2SiO_2$ or more alkaline silicates react vigorously on zinc and aluminum. The hydrogen liberated is sometimes sufficient to burst a galvanized drum which has been, in error, filled with silicate; but at ordinary temperatures and commercial concentrations the action is so slow as to be practically negligible. Zinc or aluminum powders, on account of their greater surfaces, yield appreciable amounts of gas. The more silica relative to Na_2O the less is

[31] *Sprechsaal,* **41**, 140-142 (1908).

the reaction. This is partly due to the tendency of high ratio silicates to form films on metal surfaces such as those which prevent the solutions of lead by marsh waters containing very small amounts of soluble silicates.

CALCIUM CARBONATE.

The desire to harden calcareous building stone and works of art which had weathered, led early investigators to consider the reaction between soluble silicates and calcium carbonate. Liebig and von Fuchs [32] believed that addition compounds were formed and rejected the assumption of Kuhlmann [33] that calcium silicates result at ordinary temperatures from contact of silicate solution and chalk or limestone. Ordway, Kobel, and Lemberg assert that this occurs only at elevated temperatures. An investigation by Kallauner [34] with a silicate containing:

$$Na_2O \qquad 8.40$$
$$SiO_2 \qquad 27.96$$
$$Fe_2O_3 + Al_2O_3 \qquad .09$$

developed the fact that a mixture with calcium carbonate exposed to the air developed a skin on the surface very like that which formed on the silicate without such admixture; furthermore the mixture below the top crust remained soft for a long time—there was no evidence that anything but drying was taking place.[35]

In closed vessels in atmospheres saturated with water vapor and free from carbon dioxide the slight skin which formed at first disappeared on standing, a clear demonstration that the set was not due to reaction between the silicate solution and the calcium carbonate. Controls of the silicate solution alone behaved in the same way. The mixture which set in free air absorbed CO_2. Extraction with water at ordinary temperature showed less Na_2O, not accounted for as Na_2CO_3, than was present in the solid mixture and the amount was still less when the extraction was done with boiling water, which would seem to indicate a reaction tending to produce calcium silicate, but in the conditions recited the amount was very small.

The point which has so many times been overlooked is important in this case. It makes a difference what sodium silicate is chosen. Calcium carbonate does not appreciably react with solutions of Na_2O, $4SiO_2$ at atmospheric temperatures. Suspensions of the most reactive

[32] *Liebig's Ann. Chem.*, **105**, 121 (1858).
[33] *Liebig's Ann. Chem.*, **41**, 220 (1842).
[34] *Gmelin-Kraut*, **3**, 1, 247 (1908).
[35] Kallauner, O., *Chem. Ztg.*, **33**, 1174-1175 (1909).

forms of $CaCO_3$ may be kept in closed vessels for days without thickening, but $Na_2O,2SiO_2$ when mixed in like manner begins to show changes in a few hours, and mixtures may be so chosen that after standing for two weeks in a closed container they will resist disintegration by water.[36] Such a mixture is

> 8 parts of water
> 10 parts of $Na_2O, 2SiO_2$ 59.1° Baumé, specific gravity 1.688
> 25 parts of $CaCO_3$

Mixtures with dolomite, which behaves much like calcium carbonate, were made by von Fuchs.[37] At elevated temperatures insoluble masses are easily made from silicates of various ratios, but the conditions of the reactions have not been fully explored. Barium and strontium carbonates also have similar properties.

OTHER MATERIALS.

Calcium phosphate, silica, and calcined clays were all found to produce firm masses with silicate solutions. After these had been exposed to the air for some time a soluble efflorescence appeared on the surface, which even in the case of silicates containing more potassium than sodium, proved to be pure sodium carbonate. One of the few cases in which silicates of potash are preferable to silicates of soda is where efflorescence is to be avoided.

Zinc oxide reacts most rapidly with silicates of high silica ratio but reacts with highly concentrated $Na_2O,2SiO_2$ at 200° to 300°C. Litharge, calcium oxide, magnesium carbonate, and Portland cement are useful for making silicate cements which react differently as concentration and ratio are varied. Asbestos reacts with silicate solutions which approach the composition of the metasilicate so that it is often quite impossible to determine by analysis of a plastic cement what silicate solution was used in its manufacture.

[36] From unpublished data of Philadelphia Quartz Company.
[37] *Dingler's polytech. J.*, **142**, 365-392, 427-444 (1856).

Chapter V.

Preparation.

WET METHODS.

The reactions which give rise to soluble silicates are conveniently grouped as wet and dry methods. All the hydroxides of the alkali metals stabilize silica sols and exert a solvent action on the hydrous forms of silica. Anhydrous silica such as quartz reacts much more slowly but when finely pulverized is comparatively easily dissolved by hot solutions of the hydroxides of potassium and sodium.

INFUSORIAL EARTH.

The great surface presented by infusorial earth makes it the most convenient source of silica for solution in alkaline hydroxides. Experiments reported in 1857 by von Liebig [1] introduced the wet method. The earth was first calcined to free it from organic matter which would otherwise discolor the silicate solution, and then stirred in small quantities into boiling solutions of caustic alkali and dissolved.[2] An alternative method consists in mixing the sodium or potassium hydroxide solution into a stiff paste with the infusorial earth and keeping it hot, but below 100°C., while the reaction takes place. The end of the reaction could be observed in either case by a partial clearing of the mixture which could then be diluted for the separation of a precipitate, consisting of silica and bases which form insoluble silicates, arising from impurities in the earth. Liebig added lime water to facilitate this process but it is now known that this is not necessary. He cautioned, however, against the use of milk of lime, which reacts at once with the silicate and displaces sodium. The impurities are usually in a flocculent condition but can be separated by decantation if the concentration be not above 1.25 specific gravity. A cycle consisting of a wash with fresh water, which is decanted and returned to the process when twice repeated, removes most of the soluble silicate, but the residue always

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[1] *Buchner's neues Repertorium für Pharmacie,* **6,** 64-67; *Chem. Zentr.,* **28,** 286-287 (1857).
[2] Thomas, C., Brit. Pat. 2756 (October 13, 1862).

contains a large percentage of silica. A typical residue of this sort would contain 80 per cent silica and 20 per cent as the sum of calcium, magnesium, iron, and aluminum oxides and such other bases as may have been present in the earth.

The silicate solutions may now be brought to the condition of stiff jellies by evaporation at atmospheric or reduced pressure. This reaction can be carried as far as the ratio $Na_2O, 2.75SiO_2$ at $100°C.$, i.e., in open vessels. Liebig causticized 7,415 parts crude sodium carbonate with lime and evaporated to 1.5 specific gravity. Then 120 parts of infusorial earth were stirred into the boiling liquor, which yielded 240 to 245 parts of a jelly with 52.3 to 53.5 per cent water. Two analyses of such solutions showed the following:

Silica, SiO_2	72.9	74.39
Sodium oxide, Na_2O	27.1	24.65
Mol ratio	2.76	3.09

It will be noted that the variation in ratio is considerable. This is difficult to regulate in the wet process. Silicate of potash prepared in similar fashion could be concentrated to a lower water content—about 41.5 per cent. The composition on the dry basis was the following:

Silica, SiO_2	64.1	68.98
Potassium oxide, K_2O.........	35.9	32.07
Mol ratio	2.66	3.35

The state of division of the silica, as well as the water it contains, affects the rate at which it is dissolved and the extent to which the reaction may be carried in a given time. For example, calcined infusorial earth will yield a silicate of composition $Na_2O,3SiO_2$ when digested 3 to 4 hours with 1.2 specific gravity caustic soda solution at 3 atmospheres pressure, but flint broken into pieces of about one cubic centimeter required 6 to 8 hours in 1.25 to 1.3 specific gravity caustic soda at $4\frac{1}{2}$ to 6 atmospheres pressure to give a ratio $Na_2O,2SiO_2$.

Insoluble Silicates.

The presence of impurities in the silica increases the time required to attain high silica ratios as well as the difficulty of obtaining clear solutions. Gaize, a rock which occurs in France, proved unsuitable [3] because of 7.6 per cent of oxides of aluminum, calcium, and iron. The silica was 84.5 per cent and water 6.6 per cent. Boiling of the calcined rock with a sodium hydroxide solution of 1.25 specific gravity yielded a dry silicate containing 68.7 per cent SiO_2 and 31.3 Na_2O—a molecu-

[3] Scheurer-Kestner, A., *Compt. rend.,* **72,** 767-769 (1871).

lar ratio of $Na_2O, 2.12SiO_2$. Longer boiling brought the composition to 67.98 per cent SiO_2 and 24 Na_2O, i.e., $Na_2O, 2.74SiO_2$. An effort to bring the ratio to a higher figure by the use of pressure was not successful. Somewhat better results might have been secured by the use of the rock without calcining, as hydrous silica dissolves more easily than dehydrated. Heating magnesium-bearing mineral with sodium hydroxide has also been proposed.[4] Sodium carbonate and sodium sulfate have been used with barium silicate.[5]

Hydrous forms of silica, such as freshly formed silica gel or by-product silica from the decomposition of SiF_4 by water, may, when washed nearly free of electrolytes, be dissolved in silicate of soda solutions of ratio $Na_2O, 3.3SiO_2$ at 100°C. until the ratio exceeds $Na_2O, 4SiO_2$.[6, 7]

In order to obtain clear silicate solutions by the wet process, Capitaine[8] considers it best to so choose the amount of silica that it can be completely dissolved and to allow the liquor to settle hot at 1.18 specific gravity or less. At higher concentrations or with an excess of silica the solutions are turbid and hard to purify.

SODIUM SULFIDE.

The process of Crispo and Mols[9] is designed to produce sodium metasilicate from silicates of high ratio by adding sodium sulfide and treating with steam which induces a reaction with the liberation of hydrogen sulfide. This has not attained any industrial importance. The Jaubert or Silicol process is designed to produce hydrogen but yields silicate of soda as a by-product.[10, 11] It depends on the reaction between ferrosilicon, manganosilicon, or silico spiegel with concentrated sodium hydroxide. Silicon itself would be the most convenient, but the alloys are used for reasons of economy. The temperatures are 60° to 80°C. and the silicon-bearing alloys are used in the form of turnings in order to give maximum surface. The reaction may be written in the following manner:

$$2NaOH + Si + H_2O = Na_2O.SiO_2 + 2H_2.$$
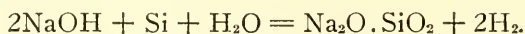
[4] Peacock, Samuel, U. S. Pat. 1,231,423 (June 26, 1917).
[5] Deguide, Camille, U. S. Pat. 1,463,037 (July 24, 1923).
[6] Phillips, John Francis, Brit. Pat. 163,877 (June 2, 1921).
[7] Phillips, John Francis, and Edward J. Rose, U. S. Pat. 1,357,183 (October 26, 1920).
[8] Capitaine, *Dingler's polytech. J.*, **222**, 363-366 (1876); abst. in *Bull. soc. chim.*, **32** [2], 27, 476-477 (1877); *Chem. News*, **36**, 82 (1877).
[9] Brit. Pat. 6,057 (March 22, 1901).
[10] *Engineering*, **107**, 103 (1919).
[11] Raney, Murray, U. S. Pat. 1,563,587 (Dec. 1, 1925).

A war time plant using this process was erected by the British Admiralty but the cost was high. Though no data are given for the compositions of the silicate solutions obtained, the process was operated to produce hydrogen and would almost inevitably yield a varying alkali-silica ratio and a solution of inferior color.[12]

Adsorbent Carbon from Rice Hulls.

The manufacture of adsorbent carbon from rice hulls is a variation of the wet process for soluble silicates.[13, 14] The rice hulls, which contain about 35 per cent silica, are first charred and then extracted with sodium hydroxide solutions. This yields a very porous structure, useful in decolorizing sugar solutions and as a gas adsorbent, but again the resulting silicate is of variable composition and usually more or less discolored with colloidal carbon and organic impurities.

Electrolysis.

The most silicious silicate solutions may be made by electrolysis of some of the sodium into a mercury cathode using a cell of the same sort as those in which caustic soda is made from salt by the Kastner process. This method is able to reduce the alkalinity of any silicate solution, but Kröger[15] found it difficult to avoid the separation of gels as the loss of sodium rendered the silica less stable. The conditions of a manufacturing operation were worked out by Codd[16] and others,[17, 18, 19, 20, 21] as a result of which a solution of $Na_2O, 3.3SiO_2$ which is easily prepared may be converted to $Na_2O, 4.2SiO_2$ which is difficult to make by other methods. Solutions of still higher ratio could be made but are too unstable to be used for the many purposes where a silicate of lower alkalinity would otherwise be desirable.

Modification of silicious silicates by the addition of sodium hydroxide and heating to hasten equilibrium has been practiced. It yields solutions of properties similar to those made by other wet methods.

[12] Caven, *J. Soc. Chem. Ind.*, **37**, 63T-67T (1918).
[13] Blardone, George, U. S. Pat. 1,293,008 (February 4, 1919).
[14] Puttaert, Jean Francois, U. S. Pat. 1,588,335 (June 8, 1926).
[15] Kröger, *Kolloid Z.*, **30**, 16-18 (1922).
[16] Codd, William Laurence, Brit. Pat. 206,572 (1923); U. S. Pat. 1,557,491 (Oct. 13, 1925); U. S. Pat. 1,562,940 (Nov. 24, 1925).
[17] Electro-Osmose Ges., Ger. Pat. 283,886 (1913).
[18] Praetorius, M., and K. Wolf, Fr. Pat. 612,486.
[19] Collins, N., U. S. Pat. 1,562,946.
[20] Silica Gel Corporation, Aust. Pat. 100,191.
[21] Lottermoser, *Kolloid Z.*, **30**, 346 (1922).

SODIUM HYDROXIDE AND SILICON CARBIDE.

Sodium hydroxide reacts in the wet way with silicon carbide, according to the equation:[22]

$$4NaOH + SiC + 2H_2O = Na_2SiO_3 + Na_2CO_3 + 4H_2.$$
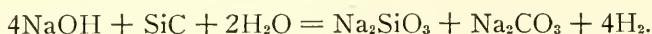
This reaction may take place at 50°C. when a 50 per cent solution of $Na_2O,2SiO_2$ is mixed with abrasive grains of silicon carbide.[23, 24]

SODIUM CHLORIDE.

Because of the economies which might result from a reaction between silica and common salt, many workers have experimented and suggested ways to bring it about.[25] Salt melts at 815°C. and boils at 1490°C. When silica is put into molten salt in a crucible no noticeable reaction takes place. Most of the salt can be distilled out of the dry mixture unchanged. If steam is introduced, some decomposition takes place and hydrochloric acid is set free. Gay Lussac and Thenard proposed this in 1809 as a step in the manufacture of soda.[26, 27, 28, 29, 30, 31]

In the ceramic industry this reaction is of interest in connection with the formation of salt glazes. This led to a study by Clews and Thompson.[32] The method chosen was to heat mixtures of approximately equal parts of finely divided silica and sodium chloride in silica tubes through which a gas stream of known composition and volume was passed. The extent of the reactions was determined by collecting the HCl and Cl_2 produced as follows:

(a) $4x\ NaCl + y\ SiO_2 + x\ O_2 = 2xNa_2O,ySiO_2 + 2xCl_2$
(b) $2x\ NaCl + y\ SiO_2 + x\ H_2O = xNa_2O,ySiO_2 + 2xHCl$
(c) $4HCl + O_2 = 2H_2O + 2Cl_2$
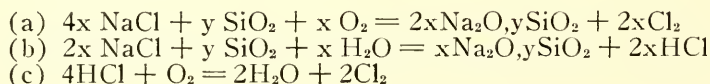
Reaction (a) took place in dry air. In moist air all three reactions occurred. There was no reaction in dry nitrogen and reaction (b) was obtained in moist nitrogen. The residues from the tubes never showed an amount of alkali equal to that calculated from the Cl and

[22] Treadwell, "Analytische Chemie," **1919-21**, Ed. 5, vol. 2.
[23] Baillio, Gervais, U. S. Pat. 1,178,205 (Apr. 4, 1916).
[24] Vail, James G., *Abrasive Ind.*, **2**, No. 6, 393-394 (1921).
[25] Natho, Ernst, Ger. Pat. 257,826 (Mar. 17, 1913).
[26] Blanc and Bazille, Brit. Pat. 8386 (1840).
[27] Fritzsche, *Wagner's Jahresbericht*, **4**, p. 118 (1858).
[28] Gossage, Brit. Pat. 2050 (1862).
[29] Ungerer, *Dingler's polytech. J.*, **197**, p. 343 (1870).
[30] Williams, Brit. Pat. 5406 (1881).
[31] Sanderval, *Compt. rend.*, **116**, 641 (1893).
[32] *J. Chem. Soc.*, **121**, 1442-1448 (1922).

HCl but this may have been due to imperfect methods of solution or an inappropriate indicator. The rate of gas flow, temperature, and moisture present affected the extent of reaction which begins at 575° to 640°C. and rises sharply just above 1000°.

TABLE 34. *Effect of Temperature on the Reaction of NaCl with SiO_2.*

Tubes 19-20 mm. dia. Rate of flow, 112 cc./hr.		Tubes 9-10 mm. dia. Rate of flow, 88 cc./hr.	
Temp.	Cc. 0.01N HCl	Temp.	Cc. 0.01N HCl
1045	41.7	1045	30.2
1010	29.5	1000	16.5
930	25.1	947	16.4
880	15.6	900	14.3
827	10.2	828	9.1
784	6.2	753	8.3
725	5.1	640*	8.0
675*	3.7	569	6.7
575	3.3		

* Lowest temperature at which solid residue was alkaline.

The reaction starts somewhere around 575°-640°C. but is still feeble at higher temperatures. Just above 1000°C. there is a marked increase in the yields. Acid obtained at the lowest temperatures may have been retained in the mixture when it was dried at 120°C.

The table given below shows the results obtained by heating 1 gram of mixture for 6 hours in tubes 9-10 mm. in diameter with 88 cc. of air per hour. Air saturated with moisture at room temperature gave far better results than dry air.

TABLE 35. *Comparison of Reaction in Dry and Moist Air.*

	Cc. 0.01N HCl			Cc. 0.01N HCl	
Temp.	Dry Air	Moist Air	Temp.	Dry Air	Moist Air
1045	30.2	100.9	753	8.3	12.3
1000	16.5	70.1	708	..	10.0
947	16.4	45.9	640	8.0	8.5
900	14.3	31.3	569	6.7	7.8
828	9.1	27.3			

The maximum yield was from a mixture heated for 36 hours to 1000°C. in moist nitrogen. It corresponded to 18.74 per cent decomposition of the salt. A study of the reaction at higher temperatures and in an atmosphere of water vapor would be interesting as both of these appear from the data obtained to make for increased yields.

Kersten [33] claims to bring about a quantitative reaction between a highly silicious silicate and salt by blowing steam into a molten bath and forming sodium metasilicate and hydrochloric acid.

[33] U. S. Pat. 1,533,009 (April 7, 1925).

DRY METHODS.

Dry methods for the preparation of soluble silicates are limited to materials of greater purity than wet methods. The latter yield solutions directly which may more or less readily be separated from insoluble impurities. But a fused silicate of soda or potash to be of service must be put into solution, which in the case of the more silicious varieties, is at best a matter of some difficulty and in the presence of more than 5 per cent alkaline earth or heavy metals becomes practically impossible.

SODIUM NITRATE.

It has been proposed to fuse silica with sodium nitrate and recover the liberated oxides of nitrogen but the reaction is not complete under any easily obtained conditions and the melt attacks refractory materials with such vigor that the process is not used.[34, 35, 36, 37]

SODIUM HYDROXIDE.

Sodium hydroxide can be used to make the silicate in the dry way. This reaction begins at lower temperatures than the other dry methods but has no industrial significance.

SODIUM SULFATE AND CARBON.

One of the first reactions used for the manufacture of silicates of soda on a commercial scale is that between sodium sulfate, carbon, and silica.[38, 39, 40, 41] It appears never to have been thoroughly investigated although it has been extensively used. A batch designed to produce a glass of the composition $Na_2O, 3.25SiO_2$ reacts at 1100°C. The surface becomes pasty[42] and is broken by characteristic eruptions or candles of burning gas which burn for a little while and subside. The use of the correct amount of carbon either as coal, sawdust, charcoal, petroleum coke, or other convenient form is important. If too much is used, a dark amber colored glass containing sulfides and colloidal carbon will result. A deficiency will leave Na_2SO_4 in the glass, an alternative which

[34] *Wagner's Jahresbericht,* **11,** 250 (1865).
[35] Brit. Pat. 2026 (1866).
[36] Brit. Pat. 2866 (1870).
[37] Brit. Pat. 2489 (1896) and 22397 (1897).
[38] Buchner, Bayer, "Kunst Gewerbebl.," **1856,** p. 645; *Wagner's Jahresbericht,* **2,** 92 (1856).
[39] Fuchs, Johann Nepomuk von, *Poly. J.,* **17,** 465-481 (1825).
[40] Peacock, Samuel, U. S. Pat. 1,425,048 (Aug. 8, 1922).
[41] Deckert, R., *Chem. Ztg.,* **72,** 535 (July, 1926).
[42] Caven, R. M., *J. Soc. Chem. Ind.,* **37,** 63T-67T (1918).

is usually accepted in practice. The fundamental reaction is assumed by Scheurer-Kestner [43] to be $2Na_2SO_4 + C = 2Na_2O + 2SO_2 + CO_2$. It is said that as much as twice the amount of carbon stated in the formula can be used without yielding sulfides in the final product. Maetz,[44] however, recommends 75 parts of Na_2SO_4 and 8 of coal to 100 of SiO_2 and a fusion temperature of 1500°C. This is a little less C than the formula and corresponds closely with the experience of the author. Scheurer-Kestner found that carbon monoxide was always present to the extent of about $\frac{1}{6}$ of the gas evolved and was also convinced that sulfur in the vapor phase is also set free, to account for which he suggests $3Na_2SO_4 + 6SiO_2 + 5C = 3S + 4CO_2 + CO + 3(Na_2O,2SiO_2)$. (Six atoms of oxygen which would yield $3SO_2$ are omitted from the right side of the equation.) His suggestion that SO_3 is liberated, then breaks down into $SO_2 + O$ which reacts with C to form CO_2, $CO + S$, does not seem tenable in view of the fact that there is no reaction between Na_2SO_4 and SiO_2 in the absence of a reducing agent. Some soda is lost by volatilizing, probably as Na_2S.

The attack of this fusion on refractory materials is very severe. The purest available form of carbon should be used, as bases introduced by the ash of coal reduce the solubility of the silicate of soda glass. The disposal of large quantities of sulfur dioxide has been urged as a serious problem; but the rate of the reaction is such that in most localities, a high stack is sufficient to disperse the gas at dilutions which are not harmful to adjacent vegetation. The manufacture of a glass of accurate composition by the sulfate process is difficult and in this country is not used for grades in which a high degree of purity or accuracy of composition is important.

Fusion of Carbonates with Silica.

Fusion of sodium and potassium carbonates with silica is the most important means of preparing alkali metal silicates.[45] In the first place, the raw materials are available in a high state of purity; secondly, they react at temperatures compatible with economical furnace operation; and thirdly, the process lends itself to accurate technical control and it yields neither offensive nor troublesome by-products.

The first study of this series of reactions was undertaken for the purpose of establishing the atomic weight of silicon. The assumption that the amount of carbon dioxide evolved was equivalent to the silica

[43] *Compt. rend.*, **114**, 117-120 (1892).
[44] Maetz, O., *Chem. Ztg.*, **42**, 569-570, 582-583 (1918).
[45] Weber, G., and J. Davidsohn, *Seifensieder Ztg.*, No. 29, 775 (1908).

present led to the false conclusion that silica was possessed of different molecular weights in different melts.[46, 47] The temperatures were not accurately controlled, but it was found that equal quantities of silica displaced varying amounts of carbon dioxide from sodium, potassium, and lithium carbonates. Scheerer[48] found that higher temperatures caused a larger evolution of CO_2 from both sodium and potassium carbonates with the same amount of silica and also that as the amount of silica increased the CO_2 released per mol SiO_2 was reduced. The speed of the decomposition was investigated by Mallard,[49] who found that for each temperature the evolution of CO_2 approached a limit, and Ebell[50] showed with successive additions of silica to molten potassium carbonate at medium red heat a series of declining values of CO_2 displaced per mol of SiO_2 added.

These observations lead to the view that in melts of alkali carbonates with silica conditions of equilibrium obtain which vary with changing temperature, time, and composition and which cannot be expressed by an equation which fixes the relation between SiO_2 and CO_2.

Wittorf[51] showed this to be the case because a melt that had come to constant weight at a given temperature above the melting point would, if placed in an atmosphere of CO_2, take up some of the gas which would be again released when, at the original temperature, air was substituted for the atmosphere of CO_2. The conditions of the experiment were not sufficiently exact to make the results entirely conclusive but the following systems were found to behave as though equilibria existed. In all except the one case cited the equilibrium was approached from one direction only, that is by loss of CO_2.

In the course of this work it was also discovered that the losses of molten carbonate in a covered crucible were negligible though they might be serious in a brisk stream of CO_2.

The reactions of potassium, sodium, and lithium carbonates with silica were studied by Niggli[52] with great care and better experimental facilities than had been available to previous workers. He chose, however, a limited set of conditions and worked between 898° and 1000° in CO_2 at a pressure of 1 atmosphere. He showed that the equilibria may be approached from either direction and that definite alkali silicates are formed. Under his conditions the amount of CO_2 displaced per mol

[46] Yorke, *Phil. Mag.*, **14**, 476 (1857).
[47] H. Rose, *Gilbert's Ann. Phys.*, **73**, 84 (1823).
[48] Scheerer, T., *Ann. Chem. Pharm.*, **116**, 149 (1860).
[49] *Ann. Chim. Phys.*, **28**, 105 (1873).
[50] Ebell, Paul, *Dingler's polytech. J.*, **228**, ser. 5, 160 (1878).
[51] Wittorf, N. M. von, *Z. anorg. Chem.*, **39**, 187 (1904).
[52] Niggli, P., *Z. anorg. Chem.*, **84**, 229-272 (1913).

TABLE 36. *Fusion of Alkali Metal Carbonates with Silica.*

Composition of Mixture After Fusion

Composition of Mixture Before Fusion	Partial Pressure CO2 0.07 Atm. % by Wt.			Mols			Partial Pressure CO2 1 Atm. % by Wt.			Mols			Temp. at Part. Pressure		Relative Increase of CO2 in Mols % by Increasing From 0.07 to 1 Atm.
	CO_2	SiO_2	R_2O	CO_2	SiO_2	R_2O	CO_2	SiO_2	R_2O	CO_2	SiO_2	R_2O	0.07 Atm.	1 Atm.	
$2Na_2CO_3 + 1SiO_2$	14.11	28.07	57.82	0.69	1	2	15.82	27.51	56.67	0.78	1	2	870°	825°	13.0
							17.70	26.90	55.40	0.90	1	2	870	780	30.4
$1K_2CO_3 + 1SiO_2$	5.05	37.06	57.89	0.18	1	1	6.73	36.45	56.87	0.24	1	1	870	780	33.0
$4Li_2CO_3 + 1SiO_2$	29.9	23.41	46.69	1.74	1	4	32.17	22.71	45.12	1.94	1	4	900	800	...
$1Rb_2CO_3 + 1SiO_2$	3.83	23.40	72.77	0.22	1	1	5.00	23.30	71.70	0.29	1	1	870	825	32.7
$1Cs_2CO_3 + 1SiO_2$	3.60	17.91	78.49	0.27	1	0.94	4.91	17.44	77.64	0.38	1	0.95	870	825	40.7

TABLE 37. *Effect of Alkali-Silica Ratio on CO_2 Remaining in Melt at 1 Atm. Pressure and 898° and 956° C.*

K_2O — SiO_2 — CO_2 (Pressure 1 Atmosphere CO_2)

Mol Ratio $K_2O : SiO_2$	898° Mol Per Cent in Melt			956° Mol Per Cent in Melt		
	K_2O	SiO_2	CO_2	K_2O	SiO_2	CO_2
1 : 0.113	49.6	5.6	44.8	. . .	. . .	. . .
1 : 0.122	49.6	6.1	44.3	. . .	. . .	. . .
1 : 0.187	49.2	9.2	41.6	49.5	9.3	41.2
1 : 0.248	49.0	12.1	38.9	. . .	. . .	. . .
1 : 0.312	48.4	15.1	36.5	49.0	15.2	35.8
1 : 0.470	47.5	22.3	30.2	48.2	21.5	29.3
1 : 0.565	46.8	26.4	26.8	47.6	26.9	25.5
1 : 0.594	46.6	27.7	25.7	47.5	28.1	24.4
1 : 0.957	43.7	41.7	14.6	44.6	42.6	12.8
1 : 0.998	43.2	43.0	13.8	44.1	44.0	11.9
1 : 1.111	42.3	47.0	10.7	43.3	48.0	8.7
1 : 1.476	. . .	. . .	. . .	39.0	57.6	3.4
1 : 2	33.3	66.7	0.0	33.3	66.7	0.0
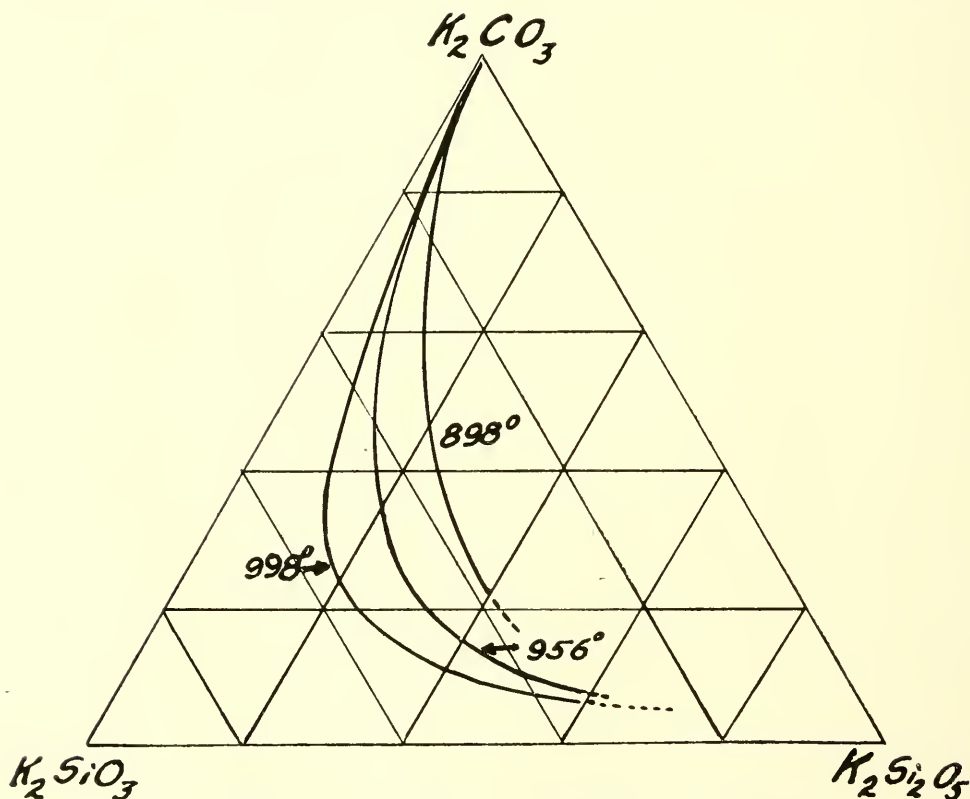
FIG. 32.—Isotherms in the System K_2CO_3, K_2SiO_3, $K_2Si_2O_5$.

of SiO_2 is greater the less the concentration of SiO_2 in the melt; but in no case did the CO_2 liberated from K_2CO_3 by silica reach a figure as high as the molecular equivalent. In a fusion of $K_2O,2SiO_2$ only half this amount is set free at 1000°. Higher temperatures and lower partial pressures of CO_2 would increase the amount of CO_2 expelled.

Potassium carbonate melts at 891° and forms with $2SiO_2$ a crystalline mass of $K_2Si_2O_5$ with a melting point of 1015° ± 10°. The melting point of K_2SiO_3 could not be determined because it could not be prepared free from carbonate and disilicate and melts of the composition K_2SiO_3 heated to higher temperatures always gave vitreous rather than crystalline masses. The proportions of carbonate, metasilicate and disilicate which remain in equilibrium at three temperatures investigated are best shown in the diagram (Fig. 32).

Small amounts of CO_2 were found in melts of K_2CO_3 with equivalent or more SiO_2 after a half hour at 1400° to 1500° in a gas furnace. Melting times employed in the manufacture of commercial silicates are much longer than this and the residual CO_2, if any is present, is so little as to escape the ordinary means of detection.

Although Niggli confirmed the findings of previous workers that the losses of both sodium and potassium carbonates were, under his conditions in a closed vessel with greater partial pressure of carbon dioxide, negligibly small, a slight decomposition does, however, take place when soda ash is heated in the air. In Niggli's experiments it amounted to less than one per cent but was slightly greater in the case of sodium carbonate than potassium carbonate. Lithium carbonate undergoes much more serious losses.

FORMATION OF CRYSTALLINE METASILICATE.

Sodium carbonate melts at 853° and a mixture containing 50 mol per cent SiO_2 gave up all its CO_2 at 1000° yielding a crystalline meta-

TABLE 38. *Expulsion of Carbon Dioxide by Silica at 898° and 956°* (Niggli).

$Na_2O - SiO_2 - CO_2$ (Pressure 1 Atmosphere CO_2)

Molecular Ratio $Na_2O : SiO_2$	898° Mol Per Cent in Melt			956° Mol Per Cent in Melt		
	Na_2O	SiO_2	CO_2	Na_2O	SiO_2	CO_2
1 : 0.085	51.7	3.9	44.4	...	...	...
1 : 0.098	51.4	4.4	44.2	51.9	4.4	43.7
1 : 0.112	51.4	5.8	42.8	51.9	5.9	42.2
1 : 0.140	51.4	7.2	41.4	...	...	...
1 : 0.143	51.3	7.4	41.3	52.1	7.6	40.3
1 : 0.191	51.7	9.9	38.4	...	...	...
1 : 0.287	...	...	...	53.3	15.7	31.0
1 : 0.302	...	...	...	53.2	16.1	30.7
1 : 0.344	...	...	...	53.6	18.6	27.8
1 : 0.353	...	...	...	53.7	19.3	27.0
1 : 0.428	...	...	...	54.2	23.9	21.9
1 : 0.495	...	...	...	54.5	27.2	18.3
1 : 1	50.0	50.0	0.0	50.0	50.0	0.0

silicate with a melting point of 1018° as determined by Niggli. Jaeger [53] had earlier determined the melting point as 1088°, which figure has been confirmed by Morey.

INDICATION OF ORTHOSILICATE.

When the melts contained more Na_2O than the metasilicate the equilibrium relations indicated an orthosilicate, formed according to the equation:

$$Na_2CO_3 + Na_2SiO_3 \rightleftarrows Na_4SiO_4 + CO_2$$
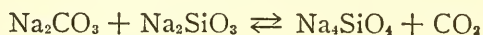
in which $1SiO_2$ displaces $2CO_2$.

DISILICATE.

When more silica than that needed to produce the metasilicate was introduced, the result was always a mixture of metasilicate and quartz.
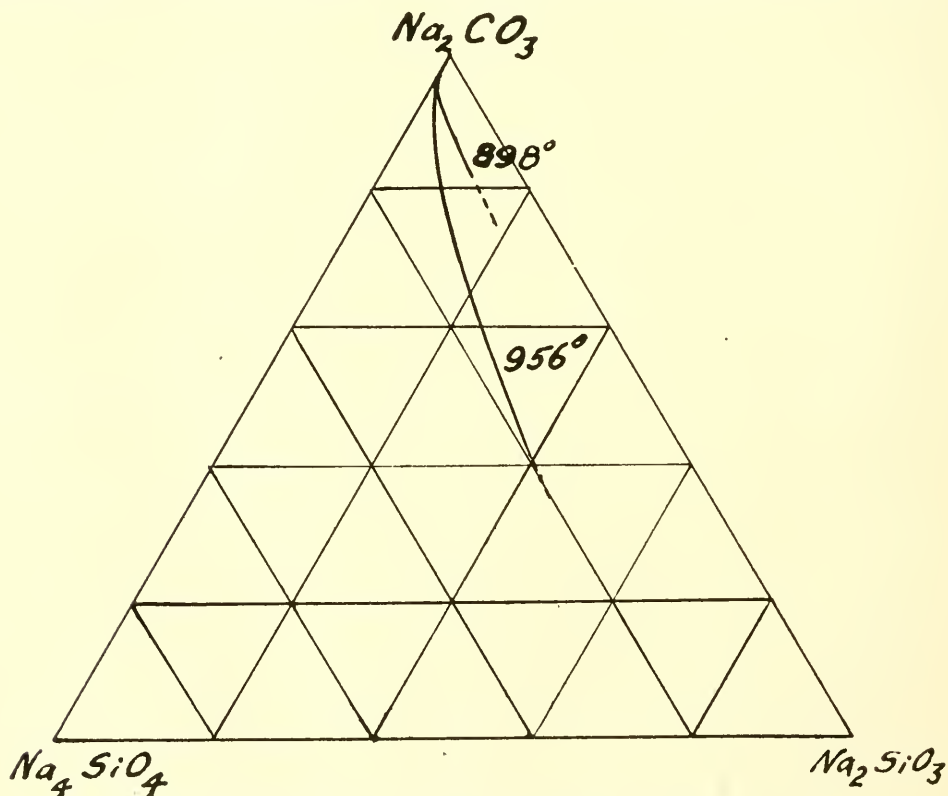
FIG. 33.—Isotherms in the System Na_2CO_3, Na_4SiO_4, Na_2SiO_3.

Wallace [54] is of the opinion that there is no higher silicate than the metasilicate in fusions but that silica in excess of this is taken up as a

[53] Jaeger, *J. Wash. Acad. Sci.*, **1**, 49-52 (1911); *J. Chem. Soc.*, **100**, II, 981-982 (1911).

[54] Wallace, R. C., *Z. anorg. Chem.*, **63**, 1-48 (1909).

solid solution. All the soluble silicate fusions made for industrial use have higher silica than this, up to four mols SiO_2 for each mol Na_2O. They are not crystalline but vitreous. It has been shown, however, that the disilicate prepared hydrothermally by Morey may exist also in anhydrous fusions.

A careful study of the system Na_2SiO_3—SiO_2 by Morey and Bowen [55] shows no evidence of silica in solid solution.

Inaccuracies in previous work on this system are in part due to failure to recognize the danger of loss of Na_2O from the melt at high temperatures which, though almost negligible after the silicate has been formed, may be serious as long as some of the Na_2O is present as carbonate. Mixtures prepared from quartz and pure sodium carbonate were held at definite temperatures until equilibrium was reached and then quenched, usually in mercury. The small amounts used could then be examined optically. This permitted the accurate determination of the points at which the system in equilibrium was all liquid and when it first contained a solid phase. Thus the following table was established.[56]

TABLE 39. *Determination of Liquids.*

Desig-nation	Analysis Na₂O	SiO₂	Mol % Na₂SiO₃	Mol % SiO₂	Melting Point	Solid Phase
2154A	50.40	49.44	99.23	0.77	1086.5	Na₂SiO₃
2330A	45.88	54.03	82.32	17.68	1031.0	Na₂SiO₃
2142A	44.92	54.93	79.27	20.73	1001.	Na₂SiO₃
2115A	39.55	....	63.42	36.58	863.	Na₂SiO₃
2512A	37.83	....	60.85	39.15	847.	Na₂Si₂O₅
2144A	37.59	62.29	58.48	41.52	859.	Na₂Si₂O₅
2510A	35.90	....	54.29	45.71	871.	Na₂Si₂O₅
2518A	34.04	....	50.03	49.97	873.5	Na₂Si₂O₅
2414A	33.99	....	49.91	50.09	873.0	Na₂Si₂O₅
2034A	33.26	....	48.44	51.69	872.5	Na₂Si₂O₅
2411A	32.83	67.25	47.32	52.68	868.	Na₂Si₂O₅
2530A	29.20	....	39.97	60.03	831.	Na₂Si₂O₅
2530B	27.32	....	36.44	63.56	802.	Na₂Si₂O₅
2530C	25.78	....	33.27	66.73	830.	High quartz
2520A	24.81	....	31.99	68.01	841.	High quartz
2429A	19.54	....	23.55	76.45	1145.	Tridymite
2429B	11.67	....	12.51	87.49	1457.	Tridymite
2431A	4.07	....	5.12	94.88	1596.	Cristobalite

The liquidus and the areas in which the various solid phases exist are shown in Figure 38, page 112.

Melts near the composition of sodium metasilicate crystallize easily so that, while glasses of this composition can be prepared in small amounts by quenching, large batches would certainly crystallize.

[55] *J. Phys. Chem.*, **28**, 1167-1179 (1924).
[56] Morey and Bowen, *J. Phys. Chem.*, **28**, 1167-1179 (1924).
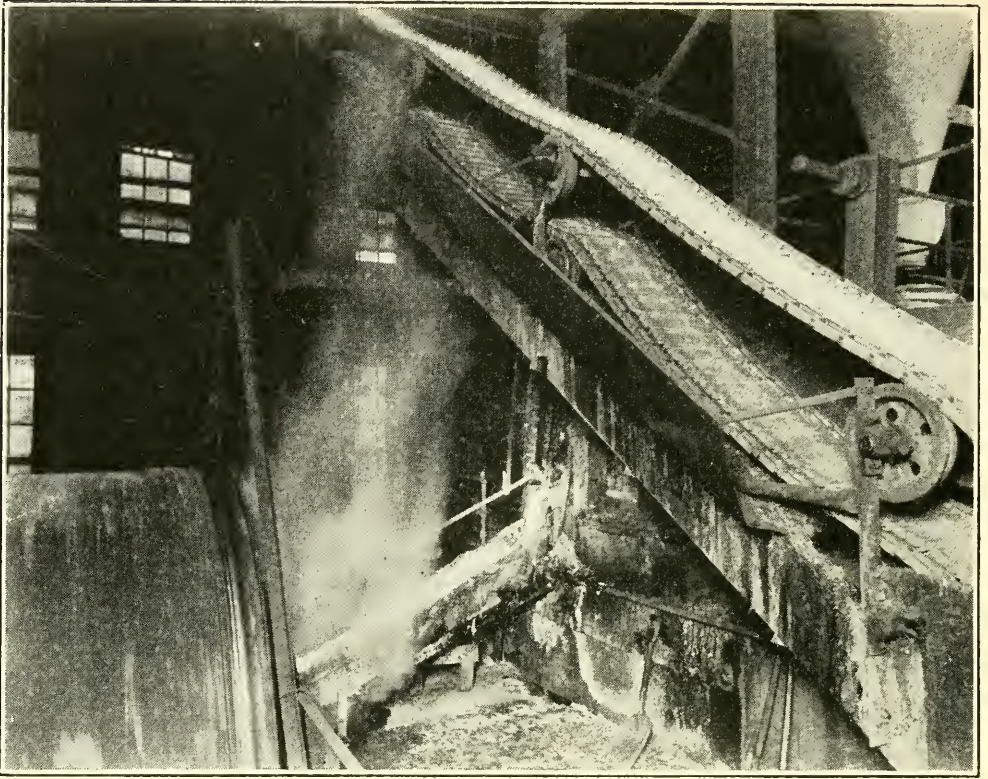
Fig. 34.—Drawing Molten Silicate of Soda Directly into Rotary Dissolver.
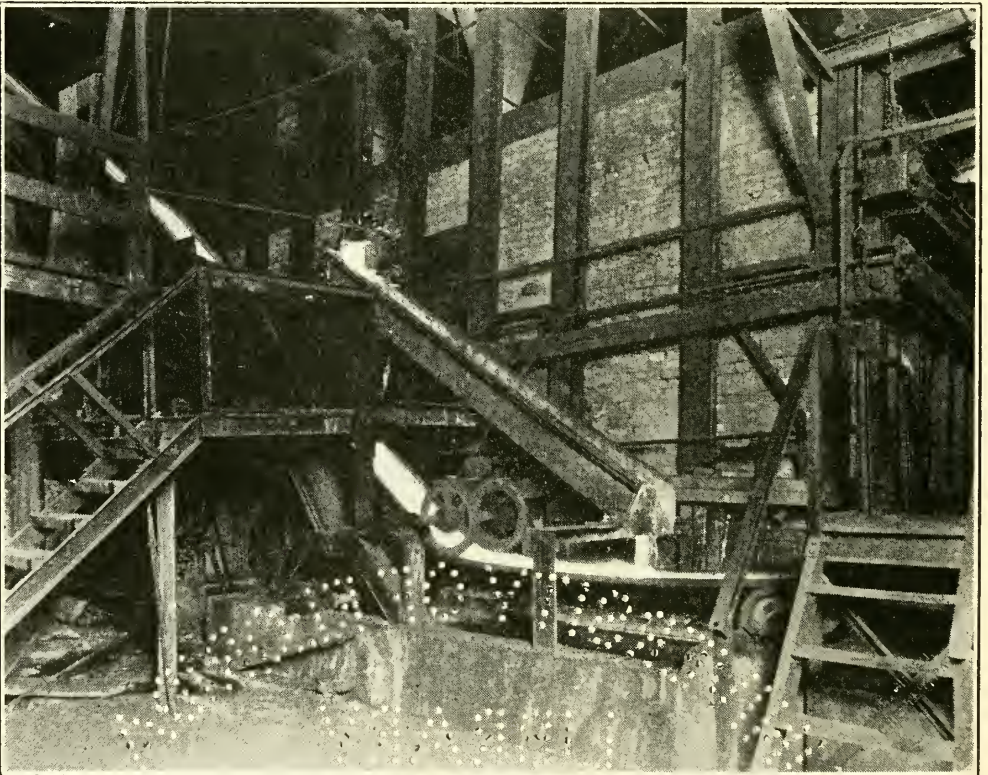
Fig. 35.—Drawing Molten Silicate of Soda on to Chain to Make Solid Glass-Like Cakes for Shipment.

Sodium disilicate is readily crystallized by heating for a few hours at the appropriate temperature, though melts of this composition remain as glasses in the ordinary course of manufacture. All the higher ratios which can be regarded as soluble are normally glasses, though Morey has obtained crystalline mixtures of $Na_2Si_2O_5$ and SiO_2 from all of them.

Fusion of Soda Ash and Silica.

On an industrial scale, soluble silicates are made by melting soda ash and silica or salt cake (Na_2SO_4), carbon, and silica in furnaces built of clay refractories. As in the glass industry, the open hearth regenerative type of furnace is most widely used,[57] although satisfactory results are also obtained from reverberatory furnaces in which coal is burned on a grate and from furnaces heated with mineral oil. The temperatures in vogue range from 1300°-1500°C., sufficient to drive out sodium chloride which is always present in the raw materials. In soda ash produced by the ammonia process, the amount is usually very small, but some of the natural sodas may contain 5 or 6 per cent. This, except from the point of view of loss, is not objectionable because it is completely expelled with the furnace gases. In the regenerative system in which the gas is cooled to temperatures below the condensation point of sodium chloride there is a tendency for this salt to accumulate, but it is found after the furnace has been shut down, as sodium sulfate, the sulfur in the fuel having been sufficient to produce enough sulfuric acid to decompose the condensed chloride.

It has been proposed to prepare soluble silicates in arc furnaces and this is entirely possible, the question being one of cost of units of heat supplied by electricity as compared with those supplied by coal, petroleum or gas. The problem of refractories, however, becomes very serious at higher temperatures for the melt contains so much silica that it readily attacks any basic refractory, and the equilibrium between silica and soda is such that highly silicious refractories fail almost equally rapidly. It would therefore appear that future developments, if they involve high temperatures, will also have to take into account the necessity of enclosing the fusion in a mass which is little reactive because it is cooled, and the economic aspect of this is likely to be discouraging.

There is, however, a great deal of room for the development of clay refractories less susceptible to solution in silicate glasses than those at present available. Water cooling is resorted to in a great many silicate

[57] Stanton, William H., U. S. Pat. 1,425,551 (Aug. 15, 1922); U. S. Pat. 1,352,700 (Sept. 14, 1920).

furnaces but unless the cooling water is needed in the process the loss of heat involved is unsatisfactorily large.

The silicate furnace differs from the glass furnace in that it is not essential for it to deliver an absolutely homogeneous product. Fine striations in the glass representing slight variations in composition seem to increase rather than retard the rate of solution.

Dissolving.

Character of the Solution.

Sodium metasilicate dissolves in water easily and completely. Silica and soda appear to go into solution at the same rates, perhaps because the whole is dissolved so rapidly. At least in a practical way one may expect a solution of the same relative composition as the solid from which it was made. Equipment like that used for dissolving other soluble salts by simple stirring or lixiviation is sufficient.

When fused sodium silicate glasses containing three or more mols of SiO_2 for each Na_2O are brought into contact with water, the phenomena are those of decomposition. Sodium goes into solution more rapidly than silica and leaves a silicious film on the surface from which it came. When a powdered anhydrous silicate of soda of the composition $Na_2O,3SiO_2$ is stirred in tenfold or larger quantity of water, the soda-silica ratio in the solution which is first formed is always in excess of the ratio existing in the glass. If the water is now replaced, the tendency is to increase the silicious layer on the surface of the glass particles and further solution is impeded. This is partly due to hydrolysis; at least the conditions which suppress hydrolysis reduce the difference between the composition of solution and solid. Solution at boiling temperature proceeds more uniformly than in the cold and small amounts of water are more effective than large.

There is no point at which a solution of $Na_2O,3SiO_2$ may be said to be saturated, as homogeneous systems of the solid and water may exist in all proportions at ordinary temperatures. A lump of the glass which has been exposed to an atmosphere of steam will, if broken across, exhibit a sharply defined outer layer which, though it retains the appearance of glass, has lost its original hardness and becomes more resilient. This outer layer contains water and may easily be dissolved in hot water though the portion which has not been hydrated is brought into solution very slowly and incompletely by similar treatment.

Morey [58] has pointed out that these solutions are very different from

[58] *J. Soc. Glass Tech.*, 6, 21 (1922).

the systems in which definite equilibria between true solutions and crystalline phases exist, and has called attention to the fact that silicate of potash appearing as a viscous liquid at ordinary temperatures may be prepared which would not be stable as a true solution below 450° to 500°. Silica must, from this point of view, be regarded as present in a colloidal condition but this does not explain the mechanism of its
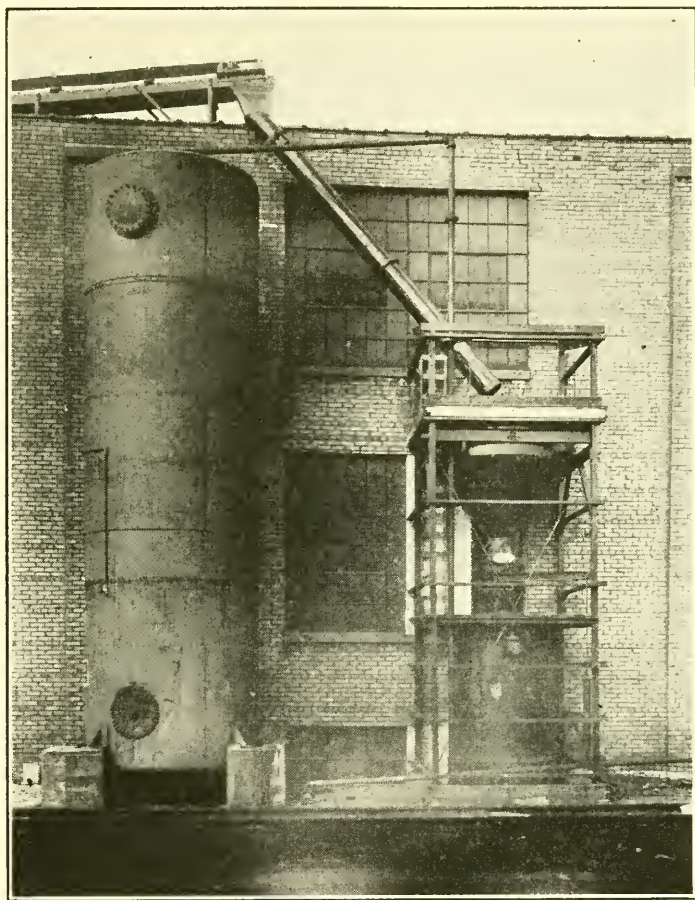
FIG. 36.—Stationary Dissolver Installation.

behavior. Whether the solution of silicates of soda and potash, like that of a high grade animal glue, necessarily goes on in two stages, the first of which is hydration and the second dispersion, has not been proven, but some hydration can be brought about and leads to the most satisfactory solutions. Industrial methods for bringing such materials into solution must provide conditions which suppress hydrolysis and favor hydration. Glasses of the composition of the disilicate or mixtures of metasilicate and disilicate dissolve without decomposition.

Apparatus for Dissolving.

The apparatus used for solution of soluble silicates [59] is of two general types. Horizontal rotary digesters operating at atmospheric or higher pressures revolve slowly so that the material to be dissolved lies in a mass at the bottom. Most of the solution takes place in this mass where, the solid being in excess, there is little tendency to decomposition and the solution, as formed, is diluted by the contact of the slowly

Fig. 37.—Stationary Dissolver Installation.

moving mass with supernatant liquor. It has been proposed to speed this reaction by grinding. Spensley and Battersby [60] introduced flints into a rotary dissolving drum, but these do not increase hydration except as they increase the surface by grinding, and hence their value is slight.

Similar conditions are secured in stationary dissolvers by packing the entire chamber with a relatively coarse glass and covering it with water. The circulation in this case must be sufficient to prevent the heavy solution which forms at first from accumulating in the bottom

[59] Taylor, E. A., U. S. Pat. 1,467,342 (Sept. 11, 1923).
[60] Spensley and Battersby, U. S. Pat. 1,176,613 (March 21, 1916).

of the vessel. If this takes place the operation is very hard to control. In either type of dissolver the solution must be removed before it becomes too viscous. Otherwise solution proceeds to a point where the whole liquid will form with the glass a mass hard enough to require a quarryman's tools for its removal and elastic enough to expel, with sufficient violence to be dangerous, a cold chisel driven into it with a sledge.[61]

Some dissolvers are charged by drawing the molten glass directly into water, and others with larger pieces which have been cooled in the air; but in all cases they must provide sufficient circulation to permit the operator to test the solution with a hydrometer and discharge it at the right time, but not enough to promote decomposition by hydrolytic action. In every case an excess of solid is used; that is, the dissolver is loaded with a larger amount of glass than can be dissolved at one charge.

[61] Stanton, William H., and James G. Vail, U. S. Pat. 1,138,595 (May 4, 1915).

Chapter VI.

Commercial Forms and Properties.

CLASSIFICATION.

Probably no product of chemical industry comes upon the market in a greater variety of forms than the soluble silicates. As the ratio of alkali to base is not limited by any stoichiometric boundaries, the number of different products is limited only by the precision with which we choose to define them. As a practical matter the limits are set by the metasilicate, Na_2SiO_3 on the side of maximum alkalinity, and the highest silica is found in a sodium silicate solution having the composition $Na_2O, 4.2SiO_2$, although still higher ratios can be secured in more dilute solutions should they be required.

Three groups of products are found: first, anhydrous silicates as glasses or powders formed by fusion processes; second, hydrous solids formed by hydration of glasses or evaporation of solutions; and third, the solutions, among which there are greater differences than is generally known.

RAW MATERIALS.

Glasses which are to be put into solution must obviously be as free as possible from bases which form insoluble silicates. The degree of purity achieved depends upon the raw materials used and upon their action on the refractory materials of the furnace. When the carbonate fusion is employed, excellent raw materials are available as may be seen from the following typical analyses of washed Ottawa sand and Solvay process soda ash. The analysis of Ottawa sand is the average of determinations made on twenty samples.

TABLE 40. *Analysis of Washed Ottawa Sand.*

	Per Cent
SiO_2	99.14
Al_2O_3	0.29
Fe_2O_3	0.07
CaO	0.28
MgO	0.09
TiO_2	0.01
Ignited Loss	0.14

TABLE 41. *Analysis of 58 Per Cent Light Soda Ash.*

	Per Cent
Na_2CO_3	99.20
$NaHCO_3$	None
NaCl	0.42
Na_2SO_4	0.016
SiO_2	0.003
Fe_2O_3	0.0011
Al_2O_3	0.0041
$CaCO_3$	0.025
$MgCO_3$	0.006
NH_3	None
H_2O	0.32
Total.............................	99.99
Na_2O	58.02
Insoluble	0.014

These are mixed and charged directly into a furnace at a temperature of about 1450°C. In the early stages of melting, most of the sodium chloride is lost as a vapor which condenses in the cooler parts of the regenerating system and is finally converted into sodium sulfate by contact with sulfur-bearing products of combustion. The specific gravity of fused soda ash is 2.43-2.51 and that of ordinary glass sand is 2.66. Reaction begins at once and copious volumes of carbon dioxide are liberated, so that there is comparatively little tendency of soda and sand to separate; but for practical reasons it is necessary to choose a sand of sufficient grain size to prevent too rapid reaction and to make batches which allow the escape of gas. Sodium carbonate melts sharply at 849°C. to a thin liquid and this results in local differences of composition which have a bearing on the behavior of the soluble glass. Products of different ratio differ in viscosity and are not easily mixed to perfect uniformity. Even small pieces of silicate glasses usually show striæ and lines of greater and less solubility due to local variations of ratio, for these variations of composition behave like the bubble in a lump of glass which can be drawn out into capillary dimensions. They form long threads in the mass as it is drawn from the furnace. The arts of the glassmaker are of course available to secure a uniform mixture, but the advantage is not commensurate with the cost.

A trifling loss of carbonate occurs due to decomposition by heat before reaction with the silica; but this is very small indeed, and after reaction with silica there is no loss from volatilization of Na_2O with the times and temperatures employed. Some loss of carbonate as dust is unavoidable but careful practice can reduce this to a very low point.

ANHYDROUS SOLIDS.

Two types only of sodium silicate glasses are well established commercially, the so-called "neutral glass" and "alkaline glass" which has the composition of the disilicate.

NEUTRAL GLASS.

The molten glass in the furnace immediately begins to attack the clay refractories of which it is made. Glasses more viscous than the soluble silicates are formed on the surface of the brick. They are also heavier and tend to accumulate at the bottom of the melt, but some are unavoidably mixed in and thus we have added to the impurities from the raw materials small amounts of alumina and iron and traces of alkaline earth metals. A typical composition of a silicate from the foregoing materials would then be:

TABLE 42. *Neutral Glass.*

$Na_2O, 3.265SiO_2$

		Per Cent
Na_2O	....	23.24
SiO_2	....	75.89
Fe_2O_3	....	0.043
Al_2O_3	....	0.195
CaO	....	0.069
MgO	....	0.069
TiO_2	........................less than	0.01
		———
		100.006

Such a glass is a clear, pale green solid of satisfactory commercial solubility though it must not be understood that it dissolves like sugar. Glasses which approximate the composition $Na_2O, 3.3SiO_2$ are known in the trade as "neutral glass". With the rise of impurities the solubility declines, or at least the time required to produce a uniform colloidal solution increases. It is, however, practical to deal with a neutral glass containing something more than one per cent of impurities. Alkaline earth metals are more objectionable than alumina. One-half per cent of calcium oxide and magnesium oxide is the maximum tolerable, while something more than one per cent aluminum oxide is permissible in a glass for making adhesive solutions. Not all sources of sand supply are equal in quality to the St. Peter sandstone which crops out in Illinois and Missouri, and the attack on refractories varies according to the composition and method of manufacture. The following analysis of "neutral glass" gives an idea of the degree of purity which is ordinarily found.

TABLE 43. *Neutral Glass.*

	Per Cent
Na_2O	23.61
SiO_2	75.31
Al_2O_3	0.38
$Fe_2O_?$	0.10
CaO	0.40
MgO	0.20

ALKALINE GLASS.

This usually appears as a yellowish glass with its iron in the ferric condition, although it is sometimes green. Both neutral and alkaline glass may be made yellow by carbon. A typical analysis of "alkaline glass" follows:

TABLE 44. *Alkaline Glass.*

$Na_2O, 2.06SiO_2$

	Per Cent
Na_2O	33.10
SiO_2	66.27
Fe_2O_3	0.036
Al_2O_3	0.199
CaO	0.098
MgO	0.071
TiO_2	Trace
Ignited loss	0.16
	99.93

GLASS MADE FROM SULFATE.

Glasses produced by the sulfate process are never equal in quality to the carbonate glasses. Sodium sulfate dissolves to about 1 per cent in the glass and can always be found in the solutions. Sodium sulfide formed by the action of some form of carbon on the sulfate is subject to serious loss by volatilization at the temperatures necessary to produce the silicate, and it attacks the refractories of the furnace with much more vigor than the carbonate batch. The composition is, therefore, difficult to control. Sulfate glasses are most successfully made in continuous furnaces permitting a slow reaction. All sulfides must be oxidized in the final glass or the solutions will be black from sulfides of iron. Sulfate glasses are usually ultramarine blue, irregular from one batch to the next and unsatisfactory for the more refined uses of the solution.

PROPERTIES.

Melting Temperatures. Morey[1] has investigated the melting temperatures of the system Na_2SiO_3—SiO_2. The soluble glasses, like the

[1] Morey, G. W., and N. L. Bowen, *J. Phys. Chem.,* **28**, No. 11, 1167 (1924).

more familiar insoluble varieties, soften gradually with rising temperature. The crystalline metasilicate shows a sharply defined melting point at 1088°C., but glasses containing more silica simply become more and more fluid with no sharp transition. Morey found, however, that there is for each composition a temperature below which a solid phase will separate if the temperature be maintained until equilibrium is reached.
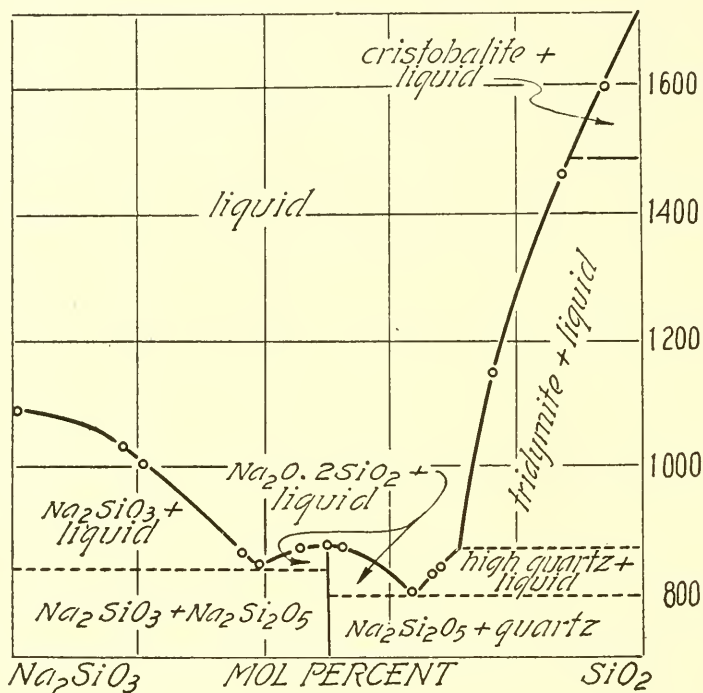
FIG. 38.

He found that Na_2SiO_3 remained the primary phase until the mixture containing 39.15 per cent SiO_2 was reached, when the disilicate, $Na_2O,2SiO_2$, appeared as the primary phase. The eutectic, located by extrapolation of the metasilicate and disilicate curves, gave a temperature of 840°C. and composition 37.5 mol per cent SiO_2.

The melting point curve of sodium disilicate is unusually flat, especially on the side toward Na_2SiO_3, 4.3 per cent excess of the latter, lowering the melting point only 2.5 degrees. When an excess of SiO_2 is added, there is a more rapid lowering of the melting point, until the disilicate-quartz eutectic is reached. The mixture with 63.56 per cent SiO_2 melts at 802.7°C. and the primary phase is $Na_2O,2SiO_2$; the mixture containing 66.73 per cent SiO_2 melts at 827°C. and high-temperature quartz is the primary phase. Both the preparations gave a eutectic temperature of 793 ± °C. Since the eutectic temperature is known,

extrapolation of the two melting point curves becomes a more reliable method of locating the eutectic composition, which is estimated as 35 mol per cent Na_2SiO_3, 65 per cent SiO_2, or 26.5 per cent Na_2O, 73.5 per cent SiO_2.

Morey found that the addition of Na_2O to silica produces a rapid lowering of the melting point, and that, unlike the oxides studied by Greig,[2] it shows no limited miscibility. The addition of 4.07 per cent Na_2O, giving a mixture containing 5.12 per cent Na_2SiO_3 and 94.88 per cent SiO_2, lowers the melting point from 1710°C., the melting point of cristobalite, to 1598°C., with cristobalite as solid phase.

His results are interesting in comparison with similar data from Jaeger and van Klooster,[3] in their study of the lithium system, and from Morey and Fenner [4] on the potassium system. The metasilicates of the three show perfect regularity in the relation of melting point to atomic weight—the melting point decreasing with increased atomic weight, while the disilicates show no such relation.

METASILICATES		DISILICATES	
Li_2SiO_3	1201°	$Li_2Si_2O_5$	1032° (incongruent)
Na_2SiO_3	1088°	$Na_2Si_2O_5$	875°
K_2SiO_3	976°	$K_2Si_2O_5$	1041°

Morey calls attention to the fact that, although there is no regularity of melting points of the disilicates, there is a striking periodicity when the shape of the disilicate liquidus is taken into consideration. Thus, the liquidus for $K_2Si_2O_5$ rises to a well-defined maximum; the metasilicate-disilicate and the disilicate-quartz eutectics for potassium are both at lower temperatures than the corresponding sodium eutectics, though the potassium disilicate melts 157 degrees higher. The sodium disilicate liquidus was found to be unusually flat, showing a difference of only 35 degrees between the temperature of the metasilicate-disilicate eutectic and the melting point of $Na_2O.2SiO_2$. And the liquidus of lithium disilicate is even flatter; the disilicate-trydymite eutectic being at 1029°C., while the temperature of decomposition of the disilicate into metasilicate and liquid is 1032°C., only 3 degrees higher. The increasing amount of flattening, in the disilicate curves, he ascribes to an increase in the amount of dissociation of the disilicate in the liquid phase. This dissociation is comparatively small in the case of potassium, is quite large for sodium, and is so great in the case of lithium that this compound is able to exist only when in contact with liquids containing

[2] Greig, J. W., *Am. J. Sci.*, 13 (Feb. 1927).
[3] Jaeger and van Klooster, *Proc. Acad. Sci. Amsterdam,* 16, 857-880 (1914).
[4] Morey and Fenner, *J. Am. Chem. Soc.,* 39, 1173-1229 (1917).

an excess of SiO_2. There is, in the dissociation of these three alkali silicates, a progressive increase in dissociation at the melting temperature with decreasing atomic weight.

Thermal Expansion. The coefficient of thermal expansion [5] for silicate of ratio $1:2 = 13.46 \times 10^{-6}$, for $Na_2O, 3.3SiO_2$ glass $= 9.17 \times 10^{-6}$. The electrical conductivity is similar to that of glass so long as water is not present. Even in concentrated solutions the resistance is very high.[*]

Refractive Indices and Specific Gravity. The refractive indices of sodium silicate glasses have been investigated by Tillotson,[6] and are given below.

TABLE 45. *Refractive Indices of Sodium Silicate Glasses.*

Silica, Per Cent by Vol.	Refractive Index
100.00	(1.464)
85.50	(1.4865)*
80.55	1.4950
78.00	1.5000
76.75	1.5000
70.70	1.5110
63.80	1.5137
54.20	1.5200

* Extrapolated.

Peddle [7] gives the following refractive index and specific gravity figures.

TABLE 46. *Composition.*

Melt	Per Cent SiO_2	Per Cent Na_2O	Per Cent $Al_2O_3 + Fe_2O_3$
A	83.00	16.58	0.42
B	76.64	22.98	0.38
C	71.20	28.44	0.36
D	66.46	33.21	0.33
E	62.32	37.37	0.31
F	58.68	41.03	0.29
G	55.42	44.30	0.28
H	52.52	47.22	0.26
K	49.91	49.84	0.25

TABLE 47. *Refractive Index.*

Melt	Refractive Index	Melt	Refractive Index
A	1.4851	F	1.5118
B	1.4952	G	1.5139
C	1.5015	H	1.5155
D	1.5056	K	1.5168
E	1.5090		

[5] English and Turner, *J. Soc. Glass Tech.,* **5**, 121-123 (1921).
[*] Cf. pp. 24-31.
[6] Tillotson, E. W., *J. Am. Ceram. Soc.,* **1**, 76-93 (1918).
[7] Peddle, C. J., *J. Soc. Glass Tech.,* **4**, 5-17 (1920).

TABLE 48. *Specific Gravity.*

Melt	Specific Gravity	Melt	Specific Gravity
A	2.353	F	2.535
B	2.413	G	2.544
C	2.457	H	2.555
D	2.495	K	2.560
E	2.521		

Solubility. The solubility of glasses containing more than two mols of silica, although it may proceed to the complete liquefaction of the solid, is nevertheless a problem in decomposition. If a "neutral glass" ($Na_2O, 3.3SiO_2$) be powdered to pass 100 mesh screen and exposed to ten times its weight of water for 12 hours, the ratio of Na_2O to SiO_2 in solution will be more alkaline than the metasilicate. A silicious layer forms on the surface of the particles which interferes with further solution. It is practically impossible to dissolve neutral glass completely even by stirring it in a large amount of hot water. A glass of the composition of the disilicate, on the other hand, dissolves with much less tendency to separate, as will appear from the following table.

TABLE 49. *Solubility of Sodium Silicates.*

Mol Ratio $Na_2O : SiO_2$ in Glass	Ratio in Solution After 12 Hrs. at 20°C. in 10 Parts H_2O	20 Parts Hot H_2O Poured through	Heated to Boiling with 20 Parts H_2O	Heated at 90° with 20 Parts H_2O 10 Min.	20 Min.	40 Min.
1 : 2.056	1 : 1.91	1 : 1.95	1 : 2.08	......	......	......
1 : 3.341	1 : 0.42	1 : 0.99	1 : 1.87	1 : 2.78	1 : 2.81	1 : 3.12
1 : 3.868	1 : 0.84	1 : 0.82	1 : 0.60	1 : 0.61	1 : 2.29	1 : 2.34

Although decomposition of this type is the rule in commercial soluble glasses at atmospheric pressures, true solubilities may be found at higher temperatures and corresponding pressures.

Morey found that glass of the composition sodium disilicate-quartz eutectic not only showed the lowest melting temperature, but in the range investigated, the greatest solubility. Thus $Na_2O, 2.8SiO_2$ with 13.1 per cent of water was completely liquid at 500°C. At such temperatures crystalline phases separate promptly in sharp contrast to their behavior at atmospheric temperatures. Proceeding to lower temperatures it was found that at 200°C. the reactions proceeded quickly with the formation of the same crystalline phases as at the melting-point curve, namely, sodium metasilicate, sodium disilicate and quartz. Other crystalline compounds appear at 60°-80°C. but have not been studied

in detail. The 125°C. isotherm shown in the chart gives some new light on solubility of sodium silicates.[8]

"Sodium metasilicate is the solid phase from D or H to E, at which point sodium disilicate appears. Since, when sodium metasilicate is dissolved in water and the solution evaporated sodium metasilicate
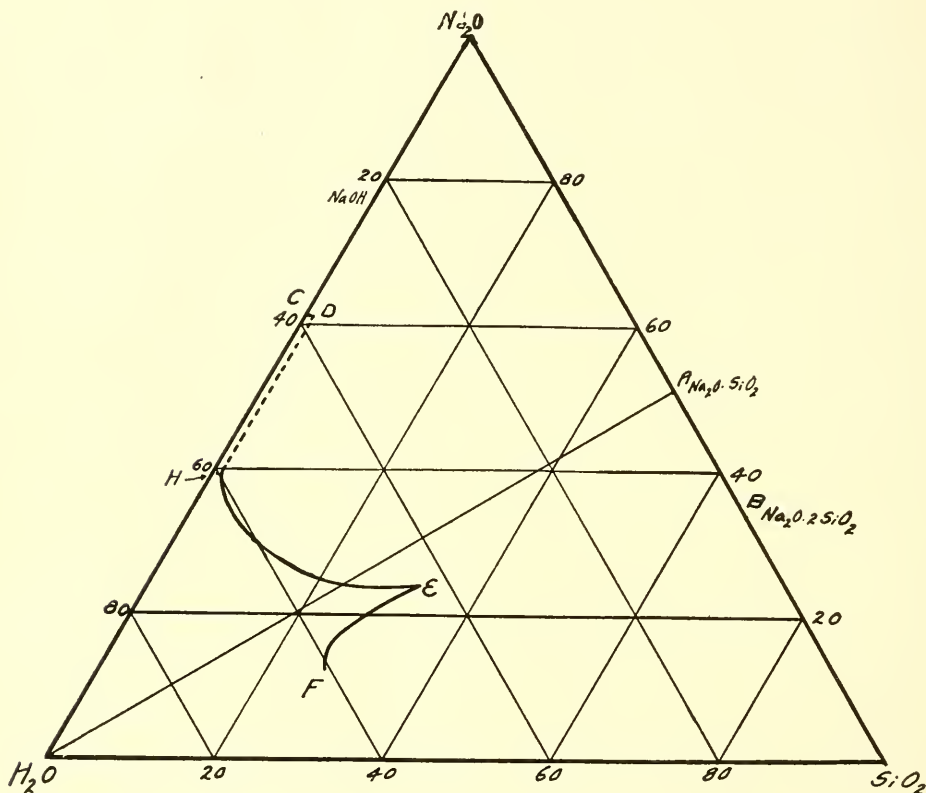
FIG. 39.—Solubility of Sodium Silicates in Water at 125° C. (Morey).

separates, as is shown by saturation curve of sodium metasilicate, HE, being cut by the tie-line H_2O-Na_2O.SiO_2, it follows that sodium meta-silicate is not decomposed by water. This is in marked contrast to potassium metasilicate, which I showed to be stable in contact with water only above 185°C. Below 185°C., potassium metasilicate is de-composed by water with formation of potassium disilicate. This difference is in the opposite direction from what one would expect from the fact that potassium is a much stronger base than sodium.

"The solubility of sodium disilicate is not greatly different from that of sodium metasilicate, and it too is stable in contact with water. This

[8] Morey, George W., personal communication (Dec. 1927).

is different from potassium, potassium disilicate being decomposed by water below 240°C.

"This isotherm, though not complete, has brought out some interesting facts. The outstanding fact is the great solubility of the sodium silicates in water. Both the metasilicate and the disilicate are to be classed among the most soluble of substances, and ordinary waterglass solutions are not as far from being stable as has commonly been supposed. The second fact, following from the first, is the unusually small increase in solubility with temperature found in these silicates. The direct comparison between 125°C. and 500°C. is not possible as yet, but it is evident that the amount of water required to dissolve a given amount of silicate is not greatly different at the two temperatures. This has an important bearing on the constitution of these solutions and the reaction taking place between the silicates and water. The third important fact that has been found is that the solubility, or the percentage of water in the saturated solution, is not greatly affected by the $Na_2O : SiO_2$ ratio in the solution, being about the same at the 18 : 1 ratio as at the 1 : 2 ratio. This is surprising, and its explanation will doubtless throw light on the constitution of these solutions. It is evident that our preconceived conceptions in regard to sodium silicate solutions require complete revision."

Hydrous Solids.

Absorption of Moisture by Glass.

Neutral glass in lump form is little altered on exposure to the air for short periods. A month of damp weather is sufficient to cause the brilliant luster of the original surface to become clouded with a film of sodium carbonate. If the surface be increased by pulverizing the glass, it absorbs moisture more rapidly and sticks together into a rock-like mass. A glass of 1 to 4 ratio may remain brilliant for a year in the climate of Philadelphia, but the "alkaline glass" is quickly clouded. The carbonating action does not, however, extend much below the surface, and a wash with cold water is sufficient to free glass which has become coated till it appears opaque from carbonate and to permit the preparation of a nearly pure silicate solution.

All the powders produced by grinding the furnace product must be stored in air-tight containers. Attempts to keep them in wooden barrels, paper cartons, or cloth sacks have all failed even when these were protected by layers of asphalt or rubber. The powders ultimately set up as hard as stone with the absorption of about 5 per cent of water.

Hydration.

Mechanism. The process of solution of these glasses seems to be the entering of water into the glass, at first in amounts so small that its glass-like character is maintained, and then increasing until fluid solutions are formed. This is clearly indicated by the experiment of placing a large lump of neutral glass into a chamber where it can be exposed to steam under pressure. At the temperature of 158.5°C., corresponding to 100 pounds steam pressure, an exposure of 15 minutes is sufficient to hydrate a layer about 2 mm. thick. If the piece be broken and an attempt made to scratch it with a steel point, a sharp line of demarcation between the hydrated outside portion and harder unaltered glass can be found, though there is no visible difference and the hydrated part, which may contain 15 per cent of water, is hard enough to cut the hand. Morey was able to make potassium silicate glasses with 8 to 25 per cent of water. These hydrated glasses are much more easily dissolved than anhydrous ones.[9] They flow at elevated temperatures, which are higher as the amounts of water decrease.

Hydration with Water. The difference between the dehydration and hydration methods is nicely shown by Schneider,[10] who pointed out that in the case of dehydration, water was removed from the existing liquid to form the solid waterglass, while the hydration method involves an addition of water to the powdered furnace glass, sufficient to render the solid material readily soluble in water. There have been various suggestions and theories concerning the amount of water to be added, the manner of its application, and the proper temperature required for subsequent heating.[11] Caven [12] emphasized as particularly important the amount of water to be used and the temperature of heating the mixture. He recommended that 2 to 3 parts by weight of water be used to 8 parts of the ground furnace glass (50 mesh) and the mixture be heated at 70°-100°C. The result was a vitreous material containing from 20 to 25 per cent moisture. Although none of the low temperature hydration methods recommended yield a solid waterglass which is completely soluble, Caven's process gives the most satisfactory product.

Hydration with Steam. Paterson [13] proposes to make a readily

[9] Henkel & Cie., Brit. Pat. 215,328 (May 14, 1925).
[10] Schneider, Louis, Address before Am. Chem. Soc., Ind. Section at Rochester (1921).
[11] Spensley, Jacob Wm., and John W. Battersby, U. S. Pat. 1,176,613 (Mar. 21, 1916).
[12] Caven, R. M., *J. Soc. Chem. Ind.*, **37**, 63T (1918).
[13] Paterson, E. A., U. S. Pat. 1,119,720 (Dec. 1, 1914).

soluble silicate of high silica ratio by exposing powdered glass of the requisite composition to the action of steam.[14] This process yields a soluble product but the mass flows and adheres tenaciously to the trays, making it inconvenient and costly. Making a solution under pressure of such concentration that it would solidify when released through a nozzle was proposed by Justice.[15] The solution must be released from the container at exactly the right concentration because the glass is dissolving rapidly and if left too long the entire charge will solidify, while if released too soon it will not become solid on blowing from the pressure vessel.

Dehydration.

Intumescence. The most satisfactory methods of making hydrous solid silicates [16] are based on drying solutions. Evaporation in trays yields lumps suitable for making the intumescent silicate of Arthur.[17, 18] When the water content of a silicate, $Na_2O, 3.3SiO_2$, is reduced to 20 per cent and it is broken into hard granules, these will, if suddenly heated to temperatures well above 100°C. (300°C. to 400°C. has been used in practice) first soften on the surface and then rapidly lose water as steam which blows bubbles in the concentrated hot liquid. The films soon lose enough water to become solid at the prevailing temperature and this process goes on until the whole is a mass of solid bubbles of 30 to 100 times the volume of the original particles. This intumescent silicate may easily be made by dropping the hydrous granules upon a hot stove and moving them about by any convenient means or by heating them in a wire mesh container such as is used for corn popping. The softening point of such an expanded material may be raised to about 525°C., by using a silicate of composition $Na_2O, 3.8SiO_2$. The thermal conductivity of this material between 25° and 300°C. is 0.00012 calory per degree centigrade per second compared with 1.01 for metallic silver. Arsem [19] obtained silica in the same form by treating the intumescent silicate with hydrochloric acid, washing and drying.

Vacuum and Atmospheric Drum Dryers. Hydrous solid silicates have been made on vacuum and atmospheric drum dryers heated by steam or other suitable means. A rotating drum is coated with a film of solution which is dried to the required degree in less than a full

[14] Gossage, William, & Sons, Ger. Pat. 210,885 (June 14, 1909).
[15] Justice, Brit. Pat. 23,391 (Oct. 23, 1911).
[16] See, for example, Rouse, Thomas, U. S. Pat. 1,109,704 (Sept. 8, 1914).
[17] Arthur, Walter, U. S. Pat. 1,041,565 (Oct. 15, 1912).
[18] Arsem, William C., U. S. Pat. 1,270,093 (June 18, 1918).
[19] Arsem, William C., U. S. Pat. 1,077,950 (Nov. 4, 1913).

revolution and scraped off with a knife.[20] The silicate is hard enough to wear the knife rapidly, making continuous attention necessary. Ratio 1 : 3.3 breaks up immediately into separate pieces, while 1 : 2 tends to come off in large sheets which are brittle only after cooling. The product of the drum dryer exposes a large surface and its irregular form is such that each particle rests on points rather than flat surfaces and so, if dried to a point where there is no danger of flowing at the temperatures encountered, it gives less trouble from sticking than forms which pack with smaller interspaces.[21, 22, 23]

Spray Drying. Edgerton [24] atomizes a silicate solution into a current of warm air and obtains a fine powder, each particle of which is
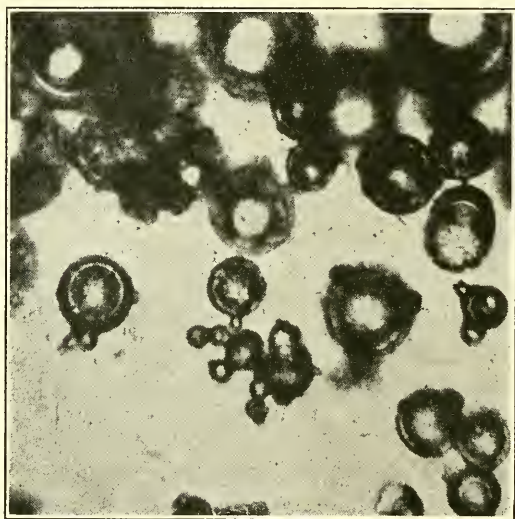
FIG. 40.—Particles of Silicate Dried by Atomizing (Magnification Approximately 250).

a more or less perfect sphere. It remains loose when kept in air-tight vessels and is easily made with uniform physical and chemical properties. This method also lends itself readily to the preparation of hydrous solids of various ratios.[25]

Other Methods. Other hydrous silicates have been proposed by Dickerson,[26] who causes drops of solution to pass through an atmosphere hot enough to cause intumescence on the surface only, and by Schnei-

[20] Dunham, Andrew A., U. S. Pat. 1,373,224 (Mar. 29, 1921).
[21] Lihme, I. P., U. S. Pat. 1,403,556 (Jan. 17, 1922).
[22] Goetschius, D. M., *Chem. Age,* **30**, No. 3, 103 (1922).
[23] Paterson, U. S. Pat. 1,119,720 (Dec. 1, 1914) ; 1,111,918 (Sept. 29, 1914).
[24] Edgerton, L. B., U. S. Pat. 1,198,203 (Sept. 12, 1916) ; 1,194,827 (Aug. 15, 1916).
[25] Clayton, William, and H. W. Richards, Brit. Pat. 203,749 (Sept. 18, 1923).
[26] Dickerson, Walter H., U. S. Pat. 1,517,891 (Dec. 2, 1924).

der,[27] who mixed powdered caustic soda (NaOH) with hydrous silica containing 1 to 4 per cent of water. He also used sodium metasilicate crystals and hydrous silica gel, drying the mass to 17.8 per cent water. Vail and Carter [28] added sodium sulfate, an efflorescent salt, to reduce the tendency of the particles to stick together.

PREFERRED METHODS OF SOLUTION.

The hydrous silicates, like the glasses, dissolve best when treated with relatively small amounts of water. The same effect is obtained if the silicate be put into a cotton sack and suspended in water. The solution escapes from the sack as formed and mixes with the water, while the residue of solid remains in contact with relatively small amounts of water. A test in which 33 grams of powder were stirred in 100 cc. of water for 15 minutes gave the following undissolved residues.

	1.	2.	3.	4.
	$Na_2O, 3.3SiO_2$	$Na_2O, 2SiO_2$	$Na_2O, 3.3SiO_2$	$Na_2O, 2SiO_2$
At 100°C.	Anhydrous	Anhydrous	17.5% H_2O	17.5% H_2O
At 100°C.	23%	1%	0.2%	0%
At 20°C.	93%	44%	36.0%	1.6%

The effect of varying amounts of water on sample 3 of the above series was determined by stirring the amounts given into 100 cc. of water, bringing to a boil and determining the residue.

Gm. in 100 cc.	Undissolved
3	16.4%
6.3	3.6
12.6	.3
25.2	.2
50.	.1

In cold water the results were:

Gm. in 100 cc.	Residue After Stirring 30 Minutes	Residue After Stirring 60 Minutes
6.3	31%	17%
12.6	20	12
25.2	12	5

PROPERTIES.

Density and Stability. Schneider studied the hydration and drying of certain silicate solutions and came to the conclusion that hydrous solids of maximum density are the most stable. They would be ex-

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[27] Schneider, Louis, U. S. Pat. 1,493,708 (May 13, 1924).
[28] Vail, James G., and John Carter, U. S. Pat. 1,139,741 (May 18, 1915).
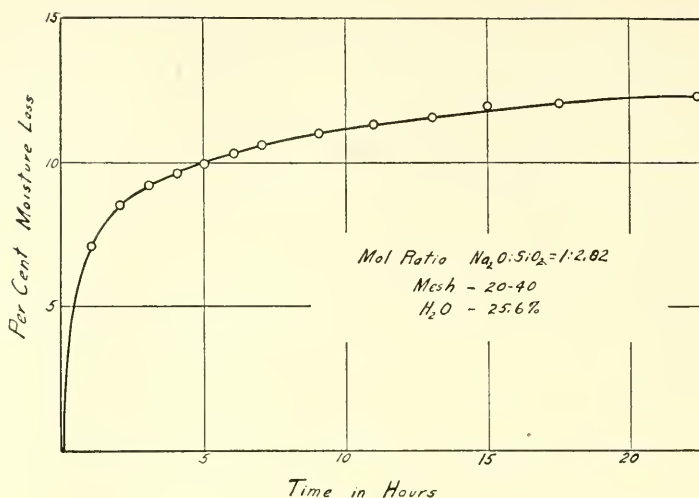
FIG. 41.—Dehydration of Hydrous Silicate at 100° Centigrade (Average of 5 and 10 Grams).
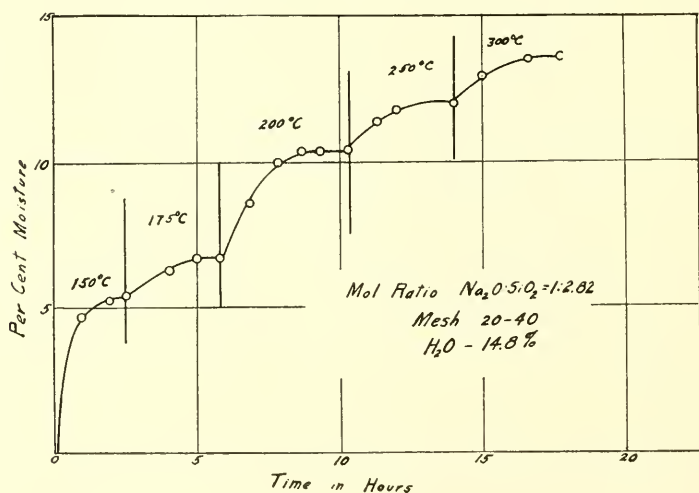
FIG. 42.—Dehydration of Solid Hydrous Silicate at Different Temperatures.

pected to be least subject to atmospheric influence because they expose the least surface.

Effect of Humidity. Schneider carried out a series of experiments designed to show the percentage moisture loss or gain of various solid waterglasses of molecular ratio 1 : 2.97, at different humidities. At the low humidities, that is, at 0 or 25 per cent relative humidity, the glasses containing the smaller percentages of water exhibited a slight tendency to take on water, while those of higher water content lost moisture rapidly. At relative humidities of 62 and 86 per cent, all of the water-

Fig. 44.—Absorption of Moisture by Hydrous Solid Sodium Silicates, 62% Relative Humidity.

Fig. 43.—Absorption of Water by Hydrous Solid Sodium Silicates, 86% Relative Humidity.

FIG. 46.—Hydrous Solid Silicates in Air, 25% Relative Humidity.
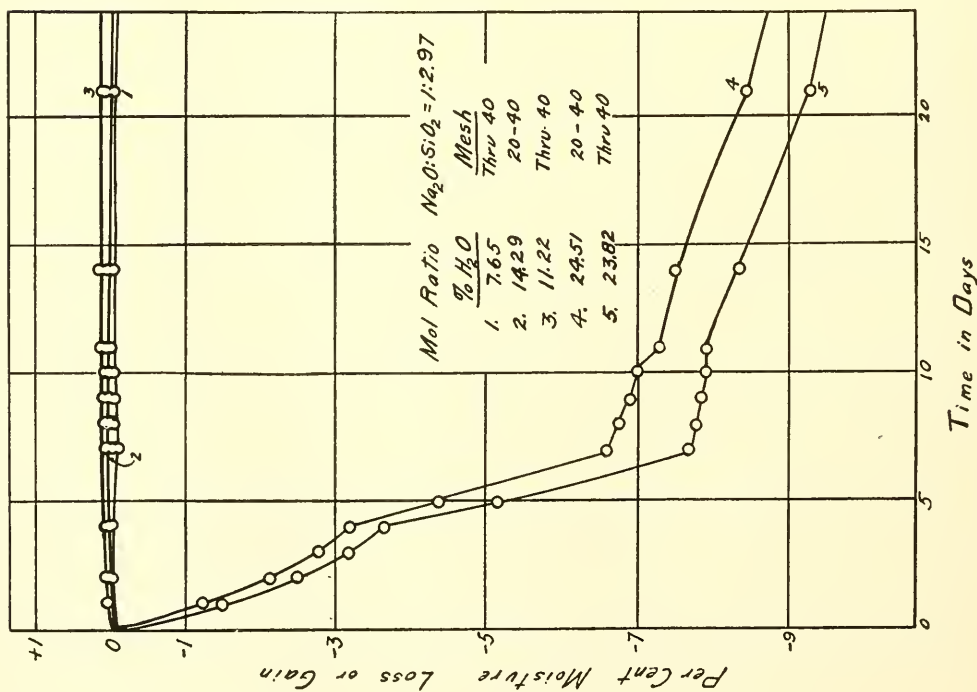
FIG. 45.—Hydrous Solid Silicates in Air, 0% Relative Humidity.

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glasses gained a considerable amount of water. Schneider points out that the rate of hydration or dehydration at different humidities is dependent upon the components and the percentage of these components in the waterglass.

HYDRATES OF SODIUM METASILICATE.

Sodium metasilicate is the only commercial form * which dissolves quickly and completely in a large excess of cold water. The com-
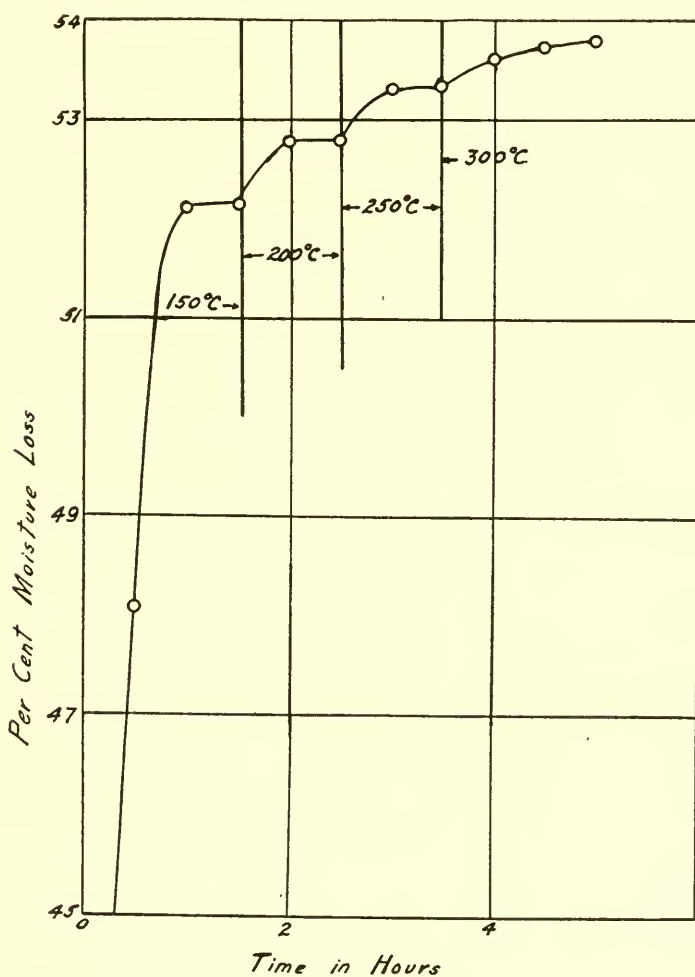
FIG. 47.—Dehydration of Sodium Metasilicate Crystals, $Na_2SiO_3.9H_2O$, at Different Temperatures.

mercial product until recently contained above 50 per cent of water and was a mixture of hydrates. Four analyses indicate between 8 and 10

* See Chapter III.

mols of water. Schneider gives data on dehydration of the ennehydrate at various temperatures.

Sodium metasilicate must be kept in tight containers, as it absorbs
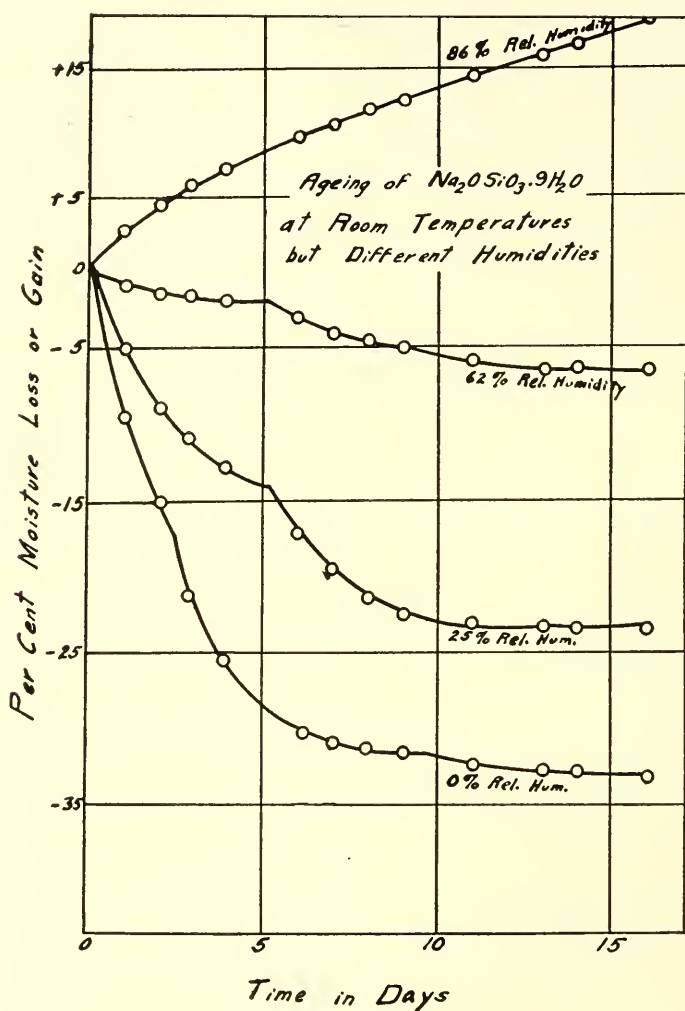
Fig. 48.—Sodium Metasilicate at Varying Relative Humidities.

or loses moisture at atmospheric temperature according to humidity. The most recent and the most stable commercial sodium metasilicate contains close to 6 molecules of water and is able to withstand temperatures up to 40°C. without caking.

SOLUTIONS.

RANGE OF RATIOS.

The sodium silicates which appear commercially in solution range from $Na_2O, 1.5SiO_2$ to $Na_2O, 4.2SiO_2$. The minimum viscosity for a

given solid content is found near the composition of the disilicate. Thus the liquid of this ratio is capable of the highest concentration, although the ratio 1 : 1.5 is regularly sold at 70° Baumé and it is not convenient to carry any silicate above this point. All the solutions within this range have more or less glue-like characteristics. Unlike the glasses, there are grades in use representative of the whole scale of gradations from maximum silica to maximum alkali. The limit is set in the first instance because of the low solubility and hence low concentration, and in the second by the fact that highly concentrated solutions containing more Na_2O will, under some conditions, show hardening due to separation of metasilicate.

CLARITY.

The solutions made from glass are always more or less opalescent. The amount of suspended matter is usually very small and may be removed by a sufficiently fine filter. This is a simple matter with or without filter aids if the solution be sufficiently dilute. Clear concentrated solutions can then be prepared by evaporation or by the method of flocculation [29] of the suspended matter at a higher concentration and settling. Filtration of silicate solutions sufficiently concentrated to have a syrupy consistency is either very slow or unsatisfactory in that a flocculent precipitate gathers in the filtrate on standing and mars the brilliant clarity of the fresh solution. On this account it is usual to filter silicate solutions below 20° Baumé and concentrate them to the desired degree by evaporation either in open vessels or under reduced pressure. The small increase in boiling point renders evaporation under atmospheric pressure less wasteful than would be the case with crystalloid compounds which require much higher temperatures for concentration. Solutions not required to be brilliantly clear are almost always brought to the requisite concentration by a saturation process.

PROPERTIES.

Specific Gravity. *Baumé Hydrometers.* The Baumé hydrometer is the universal measure of silicate concentrations in the United States and in continental Europe. The Twaddell scale is used in England. The Baumé scale being an arbitrary one, several variations have come into

[29] Vail, James G., and John Carter, U. S. Pat. 1,132,640 (March 23, 1915).

use. That sanctioned by the U. S. Bureau of Standards for liquids heavier than water bears the following relation to specific gravity:

$$\text{Sp. gr.} = \frac{145}{(145 - {}^{\circ}\text{Baumé})}$$

$${}^{\circ}\text{Baumé} = 145 - \frac{145}{\text{sp. gr.}}$$

Hydrometer Errors. It should be pointed out that hydrometers used in viscous silicate solutions are more liable to error than those used in most salt solutions. If any, of the liquid gets on the stem above the point at which it comes to rest it may dry and depress the reading by weighting the instrument and yet escape notice because it is transparent. For the same reason hydrometers are not always well cleaned after use. They should be washed with clean water until no alkali is detected by taste—a homely but effective test. Silicate hydrometers are often kept under water when not in use. This is effective from the point of view of preventing the accumulation of silicate on the glass, but instruments used in this way should be frequently checked as they tend to lose weight and give heavy readings due to the solvent action of alkaline waters on the glass. Heavy hydrometers with short ranges are most satisfactory because they come to rest more quickly in syrupy solutions. Care is required to prevent the formation of a surface skin on the solution which may prevent the hydrometer from sinking to its proper level. It is sometimes permissible to place two or three drops of water on the surface of the sample shortly before the hydrometer comes to rest in cases where the sample is not to be further examined. Viscosity readings would be worthless after adding even the most trifling amounts of water.

Relation to Composition. The total solids in a silicate solution are not indicated by the hydrometer reading unless the ratio of alkali to silica is known, as will appear from the following data from Stericker, which have been checked by other workers and shown to be reliable.

Fig. 49.— Baumé Hydrometer.

TABLE 50. *Total Solids vs. Baumé for Various Ratios—(Continued).*

Per Cent Na$_2$O	Per Cent SiO$_2$	Total Solids	Baumé	Specific Gravity
				Na$_2$O, 3.9SiO$_2$
6.79	25.75	32.54	34.0	1.3063
6.62	25.11	31.73	33.7	1.3028
3.95	14.98	18.93	20.6	1.1656
3.51	13.31	16.82	18.2	1.1435
2.99	11.34	14.33	15.6	1.1206
2.48	9.41	11.89	13.0	1.0985
1.99	7.55	9.54	10.5	1.0781
1.50	5.69	7.19	8.0	1.0584
.99	3.75	4.74	5.5	1.0394
.49	1.86	2.35	2.7	1.0190
				Na$_2$O, 3.36SiO$_2$
9.12	29.76	38.88	42 0	1.4078
9.00	29.37	38.37	40.7	1.3902
8.50	27.74	36.24	39.1	1.3692
8.04	26.24	34.28	37.4	1.3476
7.47	24.38	31.85	34.9	1.3170
6.88	22.46	29.34	32.0	1.2832
6.49	21.18	27.67	30.4	1.2653
5.97	19.49	25.46	28.1	1.2404
5.08	16.58	21.66	23.5	1.1934
4.03	13.15	17.18	18.9	1.1137
3.03	9.89	12.92	14.8	1.1499
2.06	6.72	8.78	9.9	1.0733
,.55	1.80	2.35	2.6	1.0183
				Na$_2$O, 2.44SiO$_2$
11.98	28.39	40.37	45.2	1.4529
11.40	27.00	38.40	43.1	1.4230
10.82	25.64	36.46	41.2	1.3969
10.20	24.17	34.37	39.8	1.3783
9.25	21.92	31.17	35.7	1.3266
8.29	19.64	27.93	32.3	1.2866
				Na$_2$O, 2.40SiO$_2$
4.99	11.66	16.65	20.0	1.1600
3.02	7.06	10.08	12.4	1.0935
1.03	2.41	3.44	4.4	1.0313
.52	1.21	1.73	2.1	1.0147
				Na$_2$O, 2.06SiO$_2$
18.42	36.84	55.26	58.8	1.6821
17.20	34.40	51.60	55.6	1.6219
12.89	25.78	38.67	44.5	1.4428
12.43	24.86	37.29	42.8	1.4188
12.01	24.02	36.03	41.6	1.4023
11.55	23.10	34.65	40.3	1.3849
11.12	22.24	33.36	38.8	1.3653
10.53	21.06	31.59	37.0	1.3426
9.38	18.76	28.14	33.7	1.3028
8.43	16.86	25.29	30.5	1.2664
6.06	12.12	18.18	22.0	1.1789
4.50	9.0	13.50	17.0	1.1328
2.99	5.98	8.97	11.1	1.0829

TABLE 50. *Total Solids vs. Baumé for Various Ratios—(Continued).*

Per Cent Na_2O	Per Cent SiO_2	Total Solids	Baumé	Specific Gravity $Na_2O, 1.69SiO_2$
13.93	22.94	36.87	44.4	1.4414
13.00	21.40	34.40	41.7	1.4037
12.04	19.82	31.86	39.2	1.3705
10.14	16.70	26.84	33.2	1.2970
6.02	9.91	15.93	20.4	1.1673
4.04	6.65	10.69	14.0	1.1069
1.90	3.13	5.03	8.0	1.0584
.64	1.05	1.69	2.3	1.0161

By plotting on a sufficiently large scale it is possible to deduce by extrapolation the silica content of any commercial silicate solution of which alkali content and gravity are known. As these are much more easily determined than silica, such a chart is a great convenience for quick estimation of ratio where the greatest accuracy is not required.
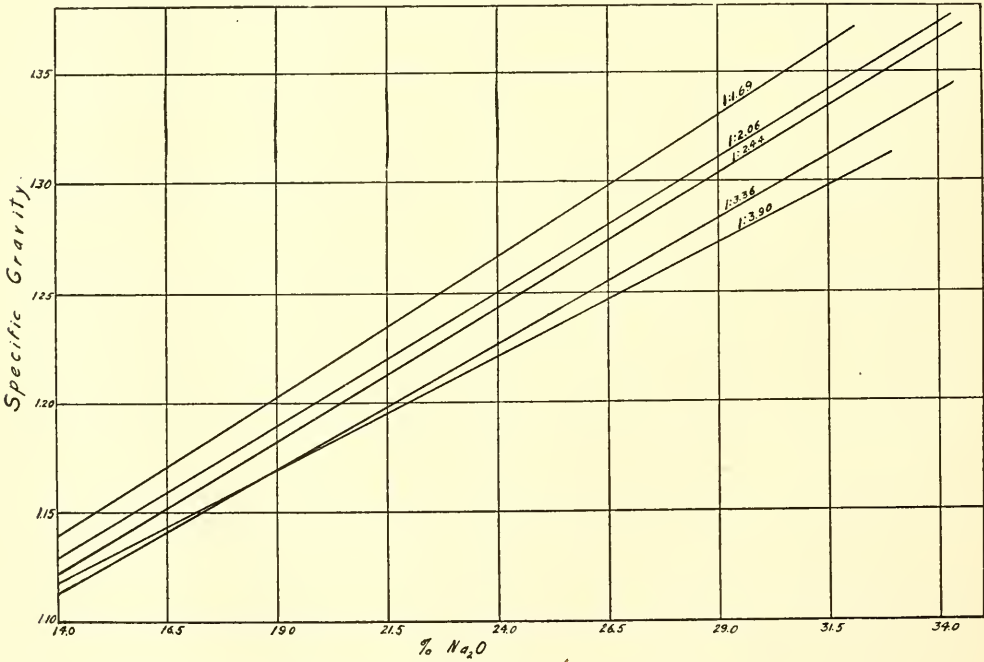
FIG. 50.—Variation of Specific Gravity with Per Cent Na_2O.
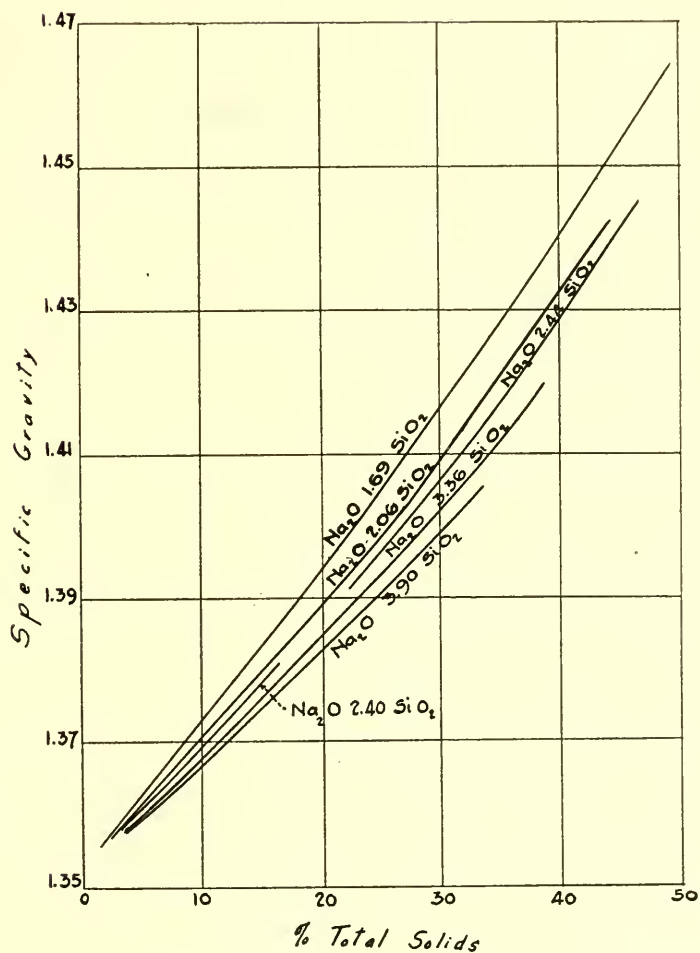
Fig. 51.—Variation of Specific Gravity with Total Solids.

Another convenient method of plotting these data is to consider the dilutions by weight and by volume of commercial solutions at their standard concentrations.
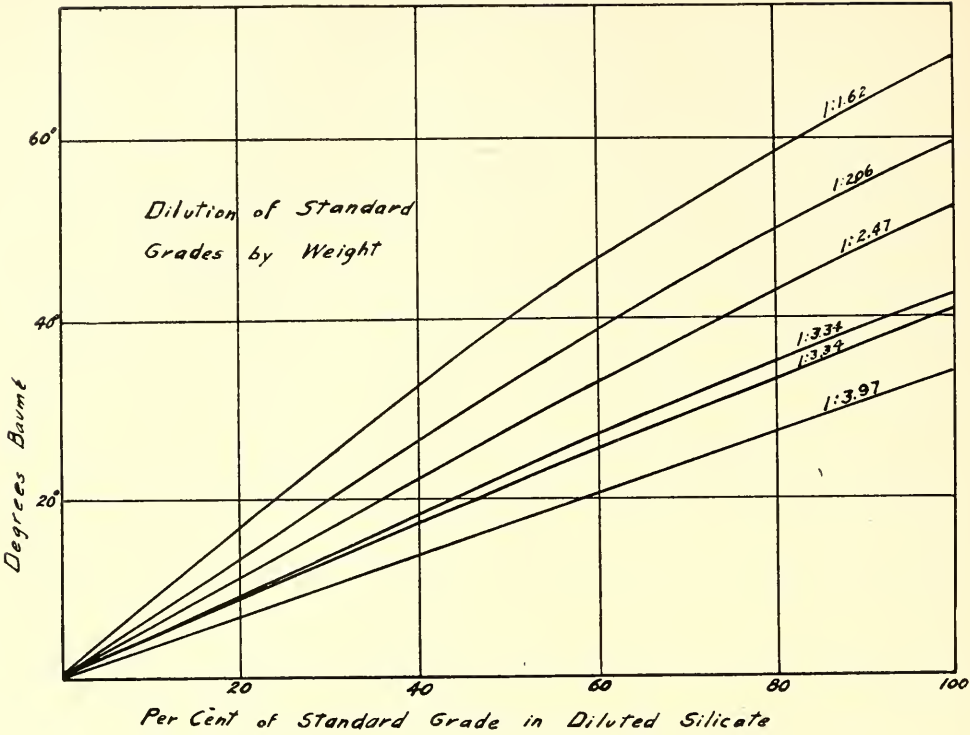
FIG. 52.—Dilution of Standard Grades by Weight.
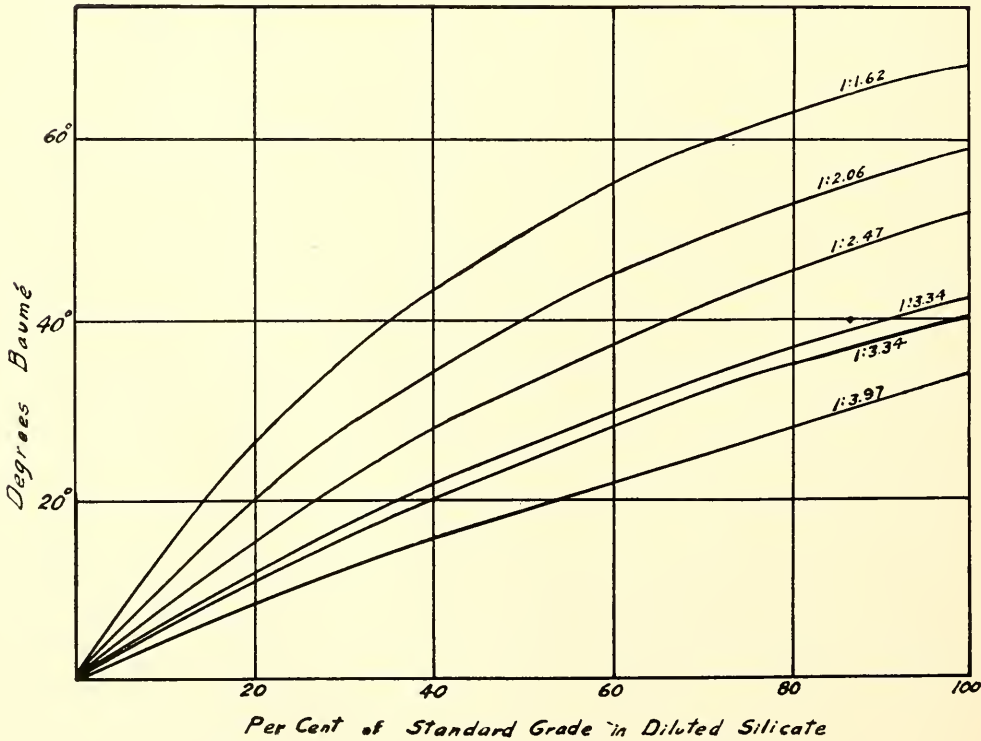
FIG. 53.—Dilution of Standard Grades by Volume.

Main [30] has shown the effect on density of increasing silica at constant Na_2O content for weight normality of sodium 1 and 3 and observed that above ratio 1 : 4 the density declines as silica is increased.

TABLE 51. *Density-Ratio SiO_2: Na_2O.*

Molecular Ratio SiO_2 : Na_2O	Conc. N_w	Density p	Conc. N_w	Density p	Conc. N_w	Density p
NaOH	1.0	1.040	2.0	1.080	3.0	1.116
1 : 2	"	1.052	"	1.101	"	1.150
1 : 1	"	1.062	"	1.123	"	....
2 : 1	"	1.075	"	1.147	"	1.217
2.5 : 1	"	1.085	"	1.168	"	1.247
3.0 : 1	"	1.099	"	1.190	"	1.274
3.3 : 1	"	1.105	"	1.195	"	1.276
3.8 : 1	"	1.111	"	1.208	"	1.296
3.95 : 1	"	1.113	"	1.207	"	1.295
4.2 : 1	"	1.109	"	1.205	"	....

Specific gravity of sodium silicate solutions is not directly proportional to concentration but at high concentrations the density is greater than would be expected from projecting the parts of the curves representing dilute solutions. This may be due to the beginnings of structural arrangement of colloidal silica in these highly viscous liquids as suggested in Chapter II.

Variation with Temperature. The variation of specific gravity with temperature has not been fully investigated, but as the most viscous solutions must be tested hot it is a matter of importance. The more concentrated the solution the smaller is its coefficient of expansion, as indicated by the following table.

TABLE 52. *Baumé Changes with Temperature.*

Water		Na_2O, $3.34SiO_2$, dil. to 20° Baumé	
Temp. °C.	Degrees Baumé	Temp. °C.	Degrees Baumé
0	.01	0	20.7
5	.00	20	20.0
10	.03	90	16.3
20	.36	100	15.4
30	.63		
40	1.13		
50	1.75		
60	2.41		
70	3.29		
80	4.20		
90	5.20		
100	6.29		

[30] Main, V. R., *J. Phys. Chem.,* **30**, 541 (1926).

TABLE 52. *Baumé Changes with Temperature—(Continued).*

Na_2O, $3.34SiO_2$, 41° Baumé

Temp. °C.	Degrees Baumé
0.0	42.0
4.4	41.7
10.0	41.5
15.5	41.2
21.1	41.0
26.6	40.8
32.2	40.6
37.7	40.4
43.3	40.1
48.8	39.9
55.5	39.7
60.0	39.4
65.5	39.2
71.1	39.0
76.6	38.7
82.2	38.5
87.7	38.3
93.5	38.0
100.0	37.8

Na_2O, $2.61SiO_2$, 42° Baumé

Temp. °C.	Degrees Baumé
30.00	42.30
39.50	42.00
43.00	41.80
48.50	41.60
54.00	41.40
60.00	41.20
65.50	40.90
71.00	40.60
76.50	40.40
82.00	40.20
86.50	40.00
92.00	39.60

Na_2O, $2.47SiO_2$, 52° Baumé

0	52.06
10	51.82
20	51.40
50	50.30
80	49.23
90	48.83

Na_2O, $2.06SiO_2$, 50° Baumé

34.00	49.60
41.00	49.40
44.80	49.20
50.00	49.00
55.00	48.80
60.20	48.60
65.50	48.40
70.00	48.20
75.00	47.70
81.00	47.30
86.50	47.20
93.00	47.20

Na_2O, $2.06SiO_2$, dil. to approx. 40° Baumé

17	39.1
21	39.0
30	38.5
40	38.5
50	38.0
60	37.6
70	37.2
80	36.9
90	37.0

Na_2O, $2.06SiO_2$, 59.1° Baumé

35.00	59.80
45.00	59.20
50.50	59.00
55.50	58.80
61.50	58.60
67.00	58.40
71.50	58.20
77.00	58.00
85.00	57.80
88.50	57.60
91.00	57.40
95.50	57.30

Refractive Index. Stericker undertook measurements of the refractive indices of silicate solutions in an effort to gain a knowledge of their constitution. This property can be measured with a high de-
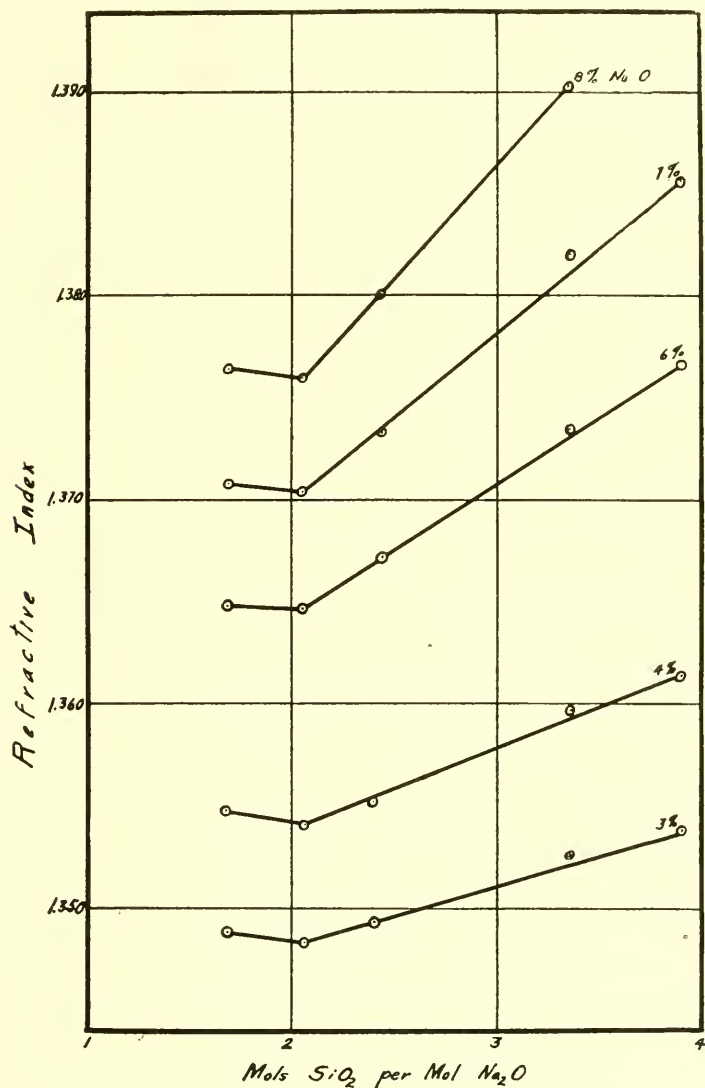
FIG. 54.—Variation of Refractive Index with Ratio at Constant Na_2O Content.

gree of accuracy and is a very useful means of detecting changes of chemical composition and arrangement. Like the conductivity data of Kohlrausch this property suggests a marked change of composition at ratio 1 : 2 as shown graphically in Figure 54.

Tables of refractive index measurements are as follows:

TABLE 53. *Refractive Index Measurements.*

Na_2O	SiO_2	H_2O *	Refractive Index
		$Na_2O, 3.9SiO_2$	
7.01%	26.59%	66.40%	1.3855
6.91	26.21	66.88	1.3844
6.79	25.75	67.46	1.3840
6.62	25.11	68.27	1.3814
6.47	24.54	68.99	1.3807
6.40	24.28	69.32	1.3800
6.30	23.89	69.81	1.3793
6.06	22.99	70.95	1.3774
5.79	21.96	72.25	1.3735
5.49	20.82	73.69	1.3718
4.64	17.60	77.76	1.3666
3.95	14.98	81.07	1.3614
3.51	13.31	83.18	1.3570
2.99	11.34	85.67	1.3538
2.48	9.41	88.11	1.3501
1.99	7.55	90.46	1.3466
1.50	5.69	92.80	1.3430
.99	3.75	95.26	1.3400
.49	1.86	97.65	1.3367
		$Na_2O, 3.36SiO_2$	
9.12	29.76	61.12	1.3997
8.50	27.74	63.76	1.3944
8.04	26.24	65.72	1.3905
7.47	24.38	68.15	1.3860
6.88	22.46	70.66	1.3809
6.49	21.18	72.33	1.3777
5.97	19.49	74.54	1.3733
5.08	16.58	78.34	1.3671
4.03	13.15	82.82	1.3609
3.03	9.89	87.08	1.3529
2.06	6.72	91.22	1.3470
1.03	3.36	95.61	1.3403
.55	1.80	97.65	1.3368
		$Na_2O, 2.44SiO_2$	
13.88	32.89	53.23	1.4247
13.36	31.65	54.99	1.4219
12.93	30.64	56.43	1.4176
12.42	29.43	58.15	1.4142
11.98	28.39	60.63	1.4100
11.40	27.00	61.60	1.4059
10.82	25.64	63.54	1.4009
10.20	24.17	65.63	1.3948
9.25	21.92	68.83	1.3883
8.29	19.64	72.07	1.3823
7.04	16.68	76.28	1.3734
		$Na_2O, 2.40SiO_2$	
4.99	11.66	83.35	1.3610
3.02	7.06	89.92	1.3495
1.03	2.41	96.56	1.3388
.52	1.21	98.27	1.3359

TABLE 53. *Refractive Index Measurements (Continued).*

Na₂O	SiO₂	H₂O *	Refractive Index
		Na₂O, 2.06SiO₂	
14.80%	29.60%	55.60%	1.4222
13.30	26.60	60.10	1.4122
12.89	25.78	61.33	1.4090
12.43	24.86	62.71	1.4043
12.01	24.02	63.97	1.4016
11.55	23.10	65.40	1.3984
11.12	22.24	66.64	1.3972
10.53	21.06	68.41	1.3916
9.38	18.76	71.86	1.3850
8.43	16.86	74.71	1.3787
7.66	15.32	77.02	1.3740
6.06	12.12	81.82	1.3651
4.50	9.00	86.50	1.3570
2.99	5.98	91.03	1.3484
1.48	2.96	95.56	1.3399
		Na₂O, 1.69SiO₂	
19.18	31.58	49.24	1.4473
18.03	29.69	52.28	1.4390
17.14	28.23	54.63	1.4337
16.10	26.51	57.39	1.4264
15.60	25.69	58.71	1.4235
15.00	24.70	60.30	1.4188
14.46	23.81	61.73	1.4157
13.93	22.94	63.13	1.4127
13.00	21.40	65.60	1.4077
12.04	19.82	68.14	1.4010
10.14	16.70	73.16	1.3886
8.10	13.34	78.56	1.3770
6.02	9.91	84.07	1.3651
4.04	6.65	89.31	1.3550
1.90	3.13	94.97	1.3425
.64	1.05	98.31	1.3358

* These figures have been obtained by difference. Small amounts of impurities, occurring as calcium, magnesium, and aluminum have been disregarded.

The graph showing the relation between refractive index and total solids shows plainly that this property can be used as a measure of concentration only when the ratio between alkali and silica is known, but it is a convenient, quick, and accurate method of control for solutions which differ only in water content.

Freezing. The difficulty of manipulating silicate solutions at high concentrations has resulted in a paucity of exact information on the freezing of silicate solutions but as their behavior at low temperatures is a matter of industrial importance some general observations must be set down. It has been pointed out that water and silicate may be present in all proportions. When the amount of water is so small that the system appears as a solid it remains clear at temperatures below the freezing point of water. It behaves like a supercooled liquid and

only becomes more brittle and glass-like. Dilute solutions, on the other hand, may be frozen.* They become opaque due to separation of ice crystals. These tend to float to the surface of any considerable body of solution in course of freezing or melting and cause a corresponding concentration at the bottom. This is very troublesome in solutions designed for uses in which exact control of concentration or viscosity is important. The degree of concentration at which crystals of water separate, i.e., the liquidus of these three-component systems, has not been studied in detail but it may be said that a 1 : 3.3 solution of 38 per cent total solids will freeze at about 28°F. (−2.22°C.), and separate, while a 54 per cent solution of 1 : 2 remains clear far below 0°F.

Frozen silicate solutions after warming and complete mixture, which is sometimes mechanically difficult on account of the gummy nature of the concentrated portion, show the same physical character as before. No case has come to the author's attention where adhesive properties were altered but this does not justify the statement that no disturbance of equilibrium takes place. A few instances of change of water resistance of silicate cements apparently attributable to freezing of silicate have been observed even in cases where the concentration was such that no separation could occur.

Boiling.   Here again the absence of much scientific data is due to experimental difficulties but some general observations are necessary to an understanding of silicates in industry.

In the first place, the colloidal character of the concentrated solutions makes it possible to boil them at temperatures much below those required for crystalline compounds.[31, 32] For instance, a solution of 63 per cent total solids, ratio 1 : 1.5, may be boiled in an open vessel at about 105°C. The more silicious solutions, 1 : 3 and above, are troublesome to boil, due to the separation of a partly dehydrated coating on the heating surface. This difficulty is negligible when working under moderately reduced pressure.

The stability of silicate solutions on boiling has to do with critical concentrations[33] above which no separation of flocculent silica takes place or even which permit the re-solution of flocculent material already separated. Failure to maintain sufficient concentrations in dissolving and evaporating equipment often gives rise to troublesome deposits. The floc when dehydrated forms a white amorphous mass very difficult to remove. The writer has seen evaporator tubes and

* Cf. pp. 40-44.
[31] Cann, Jessie Y., and Dorothy L. Cheek, *Ind. Eng. Chem.*, **17**, 312 (1925).
[32] Cann, Jessie Y., and K. E. Gilmore, *J. Phys. Chem.*, **32**, No. 1, 72 (1928).
[33] Codd, Lawrence Wm., Brit. Pat. 206,572 (Nov. 5, 1923).

pipe lines almost closed in this way. Stability is also a matter of importance when the solutions are used at high dilutions as in the textile industry, where the separation of a little floc may cause goods to dye unevenly. Carter has found that solutions prepared in different ways with the same composition vary widely in stability on dilution and heating. It is frequently found that a solution will remain clear at two concentrations as at 5° and 20° Baumé and will flocculate at intermediate points. Much remains to be learned in this realm. For purposes of control, an idea of stability may be gained by partly neutralizing a diluted silicate, heating and measuring turbidity under closely defined procedure.

Viscosity. Industrially speaking, viscosity is the most important property of silicate solutions. Beginning at the viscosity of water all silicate solutions above the ratio $Na_2O, 1.5SiO_2$ may be concentrated till they become too viscous to flow at ordinary atmospheric temperatures. The same is true at higher temperatures but the concentrations are higher. Although silicates of like viscosity may differ widely in other respects they all, except the metasilicate which crystallizes, may be brought to any viscosity within the range indicated. The curves on which viscosity changes are graphically shown give no clear evidence of the constitution of the solutions except that the more silicious ones indicate the presence of increased amounts of colloidal matter and an approach to the phenomenon of gelation.

Range. In order to visualize the flowing characteristics of silicates of various viscosities here given in centipoises it will be convenient to consider the approximate values of some other substances, more or less familiar, on the same scale at 20°C.

TABLE 54. *Comparative Viscosities.*

	Centipoises
Water	1.0050
Glycerin 80 per cent	55.34
Winter medium oil	163.
Glycerin 90 per cent	207.6
Castor oil	9.86
Heavy cylinder oil "600 W"	3,581.
Pure corn syrup	15,586.

Viscometers. Devices for measuring viscosity are many, but only a few are adapted to deal successfully with very viscous sticky liquids. Bingham [34] has pointed out that all the silicate solutions encountered industrially are viscous liquids and not plastic solids—that is, their stress flow curves pass to zero—they flow, however slight the force

[34] Bingham and Jacques, *Chem. & Met. Eng.*, 23, 727 (1923).

applied to them, though often this can be detected only after considerable lapse of time.

The only method which has been found satisfactory for the most viscous silicates is that which depends upon the rate at which a steel ball drops through a column of silicate.[35] By a somewhat involved calculation the data thus obtained can be expressed in terms of absolute viscosity. The instrument consists of a graduated glass tube, 29 cm. long and 2.5 cm. in diameter. It is conveniently held vertically in a wider tube which serves as a thermostat. The liquid, the viscosity of which is to be determined, is placed in the graduated tube, the temperature of the thermostat adjusted to 20°C., and the liquid allowed to stand until its temperature is precisely 20°C. This accurate adjustment of the temperature is important since small variations in the temperature cause large differences in viscosity. A steel square 1/16 inch in diameter is allowed to fall through the liquid and its velocity obtained by noting the time in seconds required for it to fall through a section 15 cm. long ending 5 cm. above the bottom. The density of the solution is determined either by the specific gravity bottle or by a hydrometer, and the viscosity in C.G.S. units obtained by substituting in the formula.

$$\eta = \frac{\frac{2}{9}\zeta r^2 (\alpha - \beta)}{V}$$

ζ = acceleration due to gravity 981 cm. per sec.^{2}
r = radius of sphere
α = density of sphere
β = density of liquid
V = uniform velocity in cm. per sec.

For adhesive silicates the time required for the ball to pass through a column of convenient length is too short to be easily measured with sufficient accuracy. Means must in any case be provided to avoid side or end effects by using a sufficiently wide tube, inserting the ball in the center of the surface and measuring its rate of travel through a section suitably removed from both ends.

Flow-out viscometers are suitable only for approximate shop measurements where large samples and large apertures can be used. Instruments like the Redwood, Engler, and Saybolt used in work with oils become clogged and unreliable due to the formation of a film or skin upon the surface of the silicate in the cup and, especially at higher temperatures, on the surface of the stream leaving the viscometer.

This film has a minimum effect on the instruments which depend

[35] Gibson, William H., and Jacobs, Laura M., *J. Chem. Soc.*, **117**, 472 (1920).
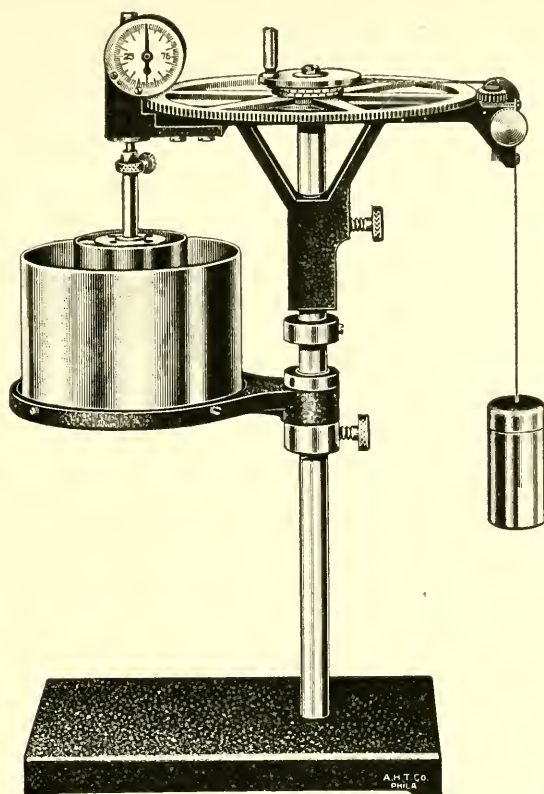
FIG. 55.—Stormer Viscometer.

on the resistance of the silicate solution to the rotation of a cylinder immersed in it. The viscometers of MacMichael, Doolittle, and
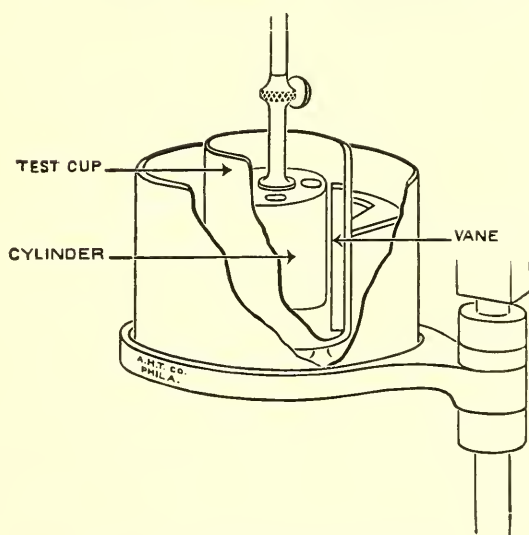
FIG. 56.—Stormer Viscometer.

Stormer are of this type. The last, on account of simplicity and convenience, has been used for the following work. It depends on the

retarding action of the silicate on the rotation of a hollow cylinder actuated by a falling weight. Duplicate readings are easily made on the latest form of this instrument if the temperature is maintained constant. The cord is wound up on the drum and a reading in seconds of the time in which the cylinder makes a hundred revolutions is taken.
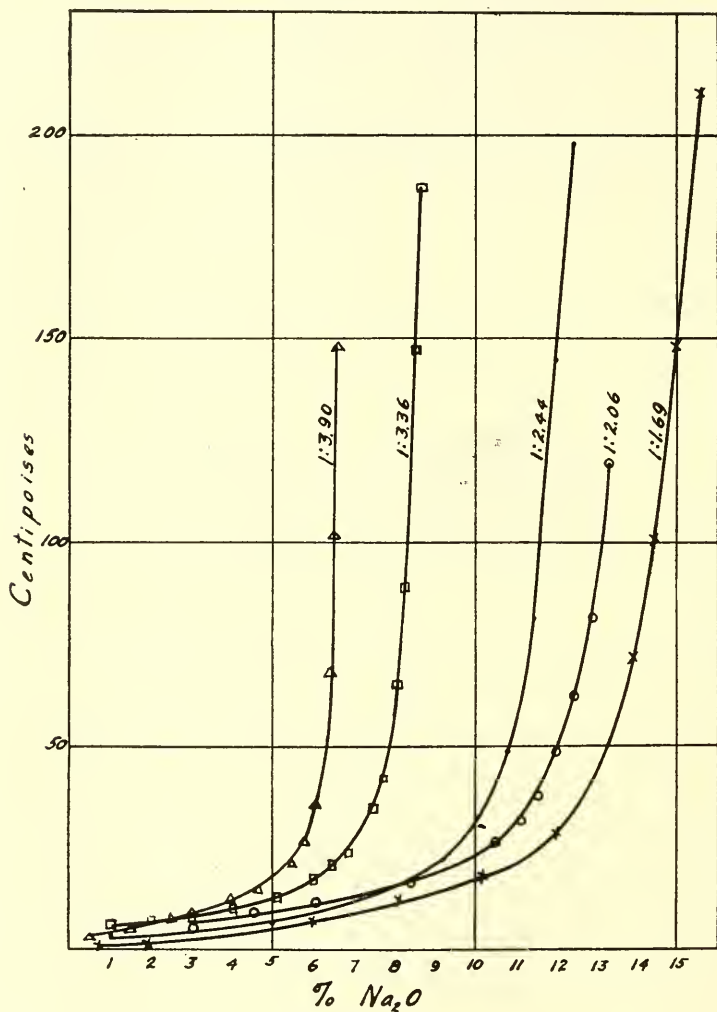
FIG. 57.—Variation of Absolute Viscosity with Na₂O.

The weight is adjustable, permitting the instrument to be calibrated to give readings on thick or thin liquids in a convenient time. Viscosity is expressed in the number of seconds required for the cylinder to make 100 revolutions. It has the additional advantage of yielding values which within the range of adhesive silicates bear a straight-line relation to viscosities expressed in absolute units. As an illustration, using our form of instrument and our calibration, V =

5.25 t — 33, between 15 and 40 Stormer seconds, and above 40 Stormer seconds, V = 3.11 t + 36 (t = time in seconds).[36]

Relation to Composition. Viscosity of silicate solutions varies with concentration, with ratio, and with temperature. The following meas-
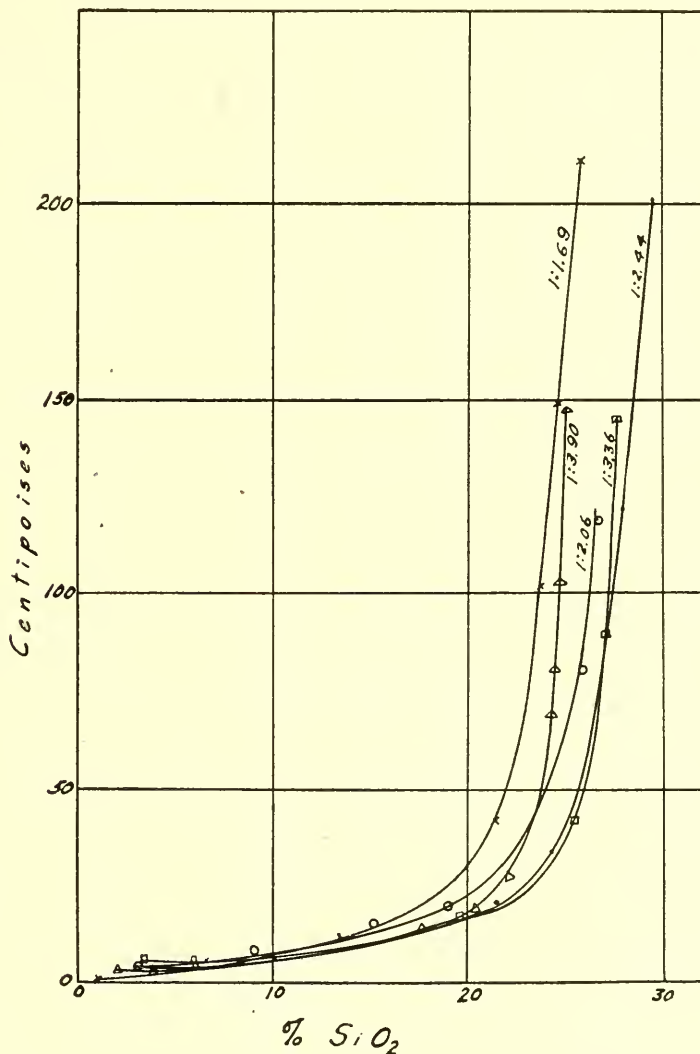
Fig. 58.—Variation of Viscosity with SiO_2.

urements [37, 38] were made on commercial solutions and may vary somewhat from perfectly pure ones.

The difficulty of making close checks with different samples, particularly in the steep part of the curves, is considerable on account of

[36] Higgins, E. F., and E. C. Pitman, *Ind. Eng. Chem.,* **12,** 587-591 (1920) ; *C.A..* **14,** 2262.
[37] Stericker, Wm., Doctor's Thesis, Mellon Inst., Pittsburgh, Pa. (1922).
[38] Dedrick, Charles H., Unpublished report of Philadelphia Quartz Company.

the large influence of small variations in composition. For example, silicate solutions take up CO_2 from the air and as far as viscosity is concerned the conversion of Na_2O to Na_2CO_3 in a silicate solution is

Table 55. *Viscosity Measurements.*

Na_2O, 3.9SiO_2

Na_2O	SiO_2	Centipoises
7.01%	26.59%	7026.0
6.91	26.21	1545.0
6.79	25.75	375.0
6.62	25.11	147.7
6.47	24.54	101.9
6.40	24.28	67.9
6.30	23.89	55.2
6.06	22.99	35.5
5.79	21.96	26.7
5.49	20.82	20.6
4.64	17.60	14.4
3.95	14.98	12.3
3.51	13.31	10.3
2.99	11.34	8.7
2.48	9.41	8.2
1.99	7.55	8.2
1.50	5.69	5.1
.99	3.75	4.1
.49	1.86	3.1

Na_2O, 3.36SiO_2

Na_2O	SiO_2	Centipoises
9.12	29.76	454.0
9.00	29.37	278.3
8.68	28.33	186.8
8.50	27.74	147.1
8.26	26.96	89.1
8.04	26.24	65.2
7.75	25.30	42.2
7.47	24.38	35.0
6.88	22.46	23.6
6.49	21.18	21.1
5.97	19.49	18.0
5.08	16.58	12.9
4.03	13.15	10.3
3.03	9.89	7.8
2.06	6.72	6.8
1.03	3.36	5.7
.55	1.80	3.1

Na_2O, 2.44SiO_2

Na_2O	SiO_2	Centipoises
13.88	32.89	1376.0
13.36	31.65	659.9
12.93	30.64	321.8
12.42	29.43	197.4
11.98	28.39	144.5
11.40	27.00	82.4
10.82	25.64	48.4
10.20	24.17	30.3
9.25	21.92	21.6
88.29	19.64	17.0
7.04	16.68	12.3

Na_2O, 2.40SiO_2

Na_2O	SiO_2	Centipoises
4.99%	11.66%	6.7
3.02	7.06	5.1
1.03	2.41	3.6
.52	1.21	1.5

Na_2O, 2.06SiO_2

Na_2O	SiO_2	Centipoises
18.42	36.84	87080.0
17.20	34.40	6115.0
15.77	31.54	835.0
14.80	29.60	341.0
13.30	26.60	119.0
12.89	25.78	81.4
12.43	24.86	62.5
12.01	24.02	49.0
11.55	23.10	38.0
11.12	22.24	32.4
10.53	21.06	25.7
9.38	18.76	21.6
8.43	16.86	17.0
7.66	15.32	15.4
6.06	12.12	12.4
4.50	9.00	9.8
2.99	5.98	6.2
1.48	2.96	4.1

Na_2O, 1.69SiO_2

Na_2O	SiO_2	Centipoises
19.78	32.58	22900.0
19.18	31.58	8496.0
18.03	29.69	1697.0
17.14	28.23	633.0
16.10	26.51	290.0
15.60	25.69	210.5
15.00	24.70	148.7
14.46	23.81	101.4
13.93	22.94	72.6
13.00	21.40	41.6
12.04	19.82	29.0
10.14	16.70	18.0
8.10	13.34	12.4
6.02	9.91	7.2
4.04	6.65	5.6
1.90	3.13	1.5
.64	1.05	.9?

Fig. 60.—Viscosity vs. Na_2O — SiO_2 Ratio for Sodium Silicate

Fig. 59.—Variation of Absolute Viscosity with Total Solids.

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equivalent to removing it. At a point where 0.1 per cent Na_2O accounts for the difference between a syrup and a jelly it is easy to see how small changes become important.
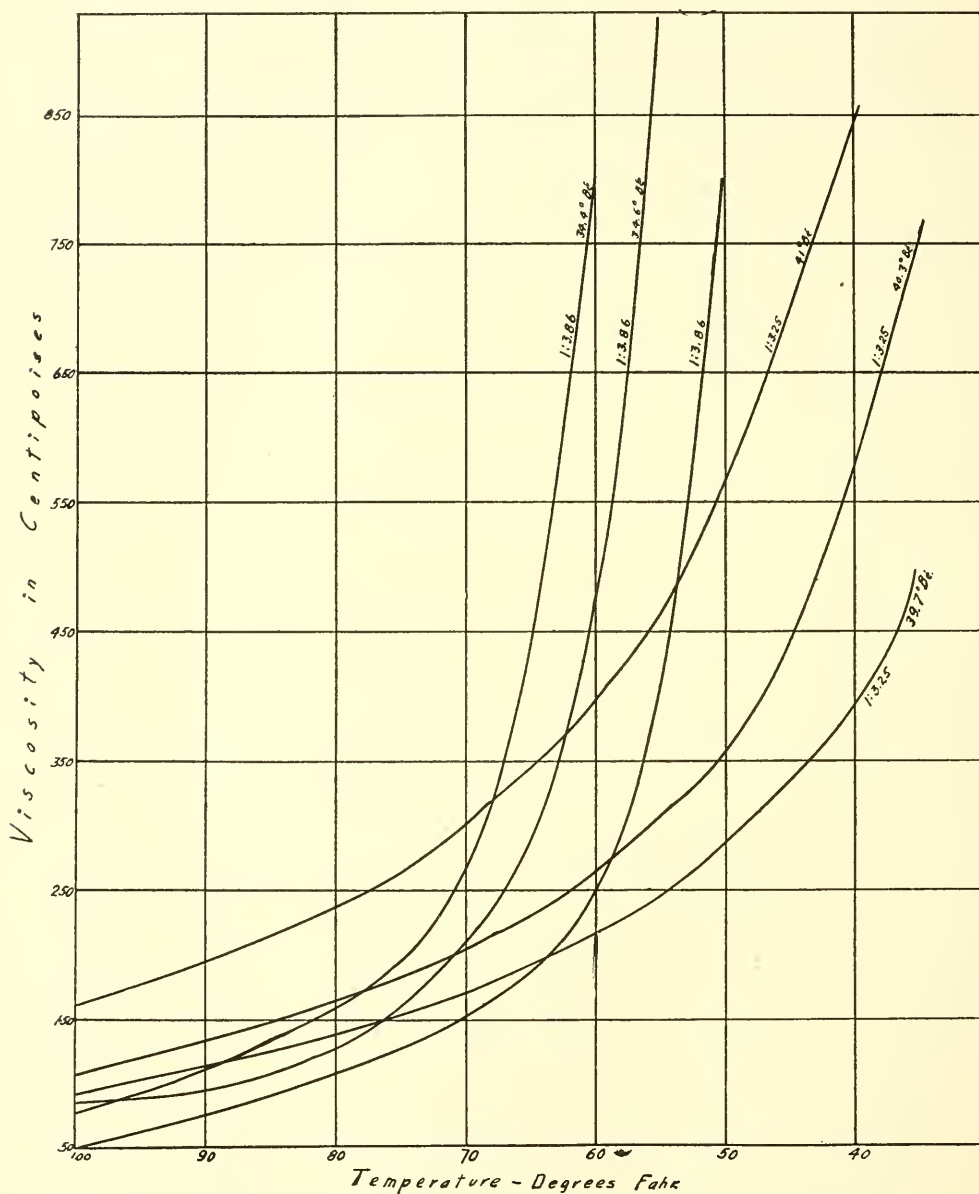
FIG. 61.—Variation of Viscosity with Temperature.

A large number of viscosity measurements were made by Main,[39] whose results are not fully satisfying because of the large differences found in working with different instruments. He points out, as Ster-

[39] Main, V. R., *J. Phys. Chem.*, **30**, 553-561 (1926).

icker [40] had done, that the curves show the properties characteristic
of lyophile sols and that the slope of the viscosity curve at a given
concentration is dependent upon the $Na_2O : SiO_2$ ratio and is greater for
the more silicious solutions. He worked with efflux type viscometers
using capillary tubes, the Ostwald, in which the liquid flows through
the tube under its own hydrostatic pressure, and the Ubbelohde vis-
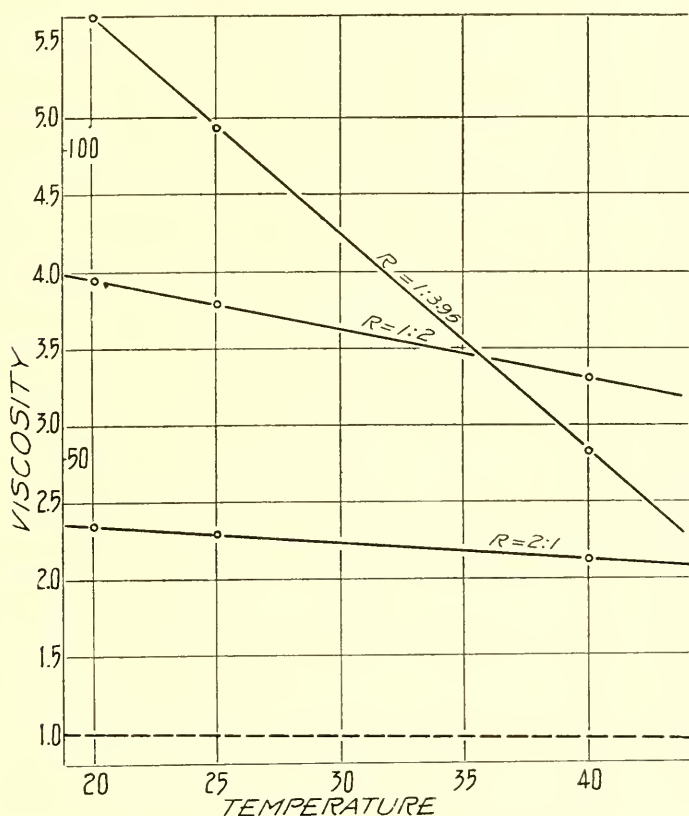
Fig. 62.—Effect of Temperature on Viscosity.

cometer, in which the liquid is forced through the capillary under a
variable pressure of gas. Neither of these instruments lends itself to
the study of high viscosities encountered in commercial silicates; they
both have high drainage errors, and the values obtained are kinematic
rather than absolute. His conclusions must therefore be considered
as applying relatively to the range between the viscosity of water
and that of the thinnest silicate which could be used for adhesive pur-
poses. The maximum specific gravity investigated was under 1.3.
Within this range it appears that the effect of temperature on viscosity

[40] Bogue, Robert H., "Theory and Application of Colloidal Behavior," New
York: McGraw-Hill Book Co., Chap. XXIV, by Wm. Stericker, 1924, p. 563.

is a straight line function, the slope of the line being dependent on the ratio as shown in Figure 62.

A series of curves in which viscosity is plotted against concentration in terms of weight normality of sodium oxide does not differ in type from those obtained at higher concentrations.

When the viscosity is plotted against ratio the minimum found by
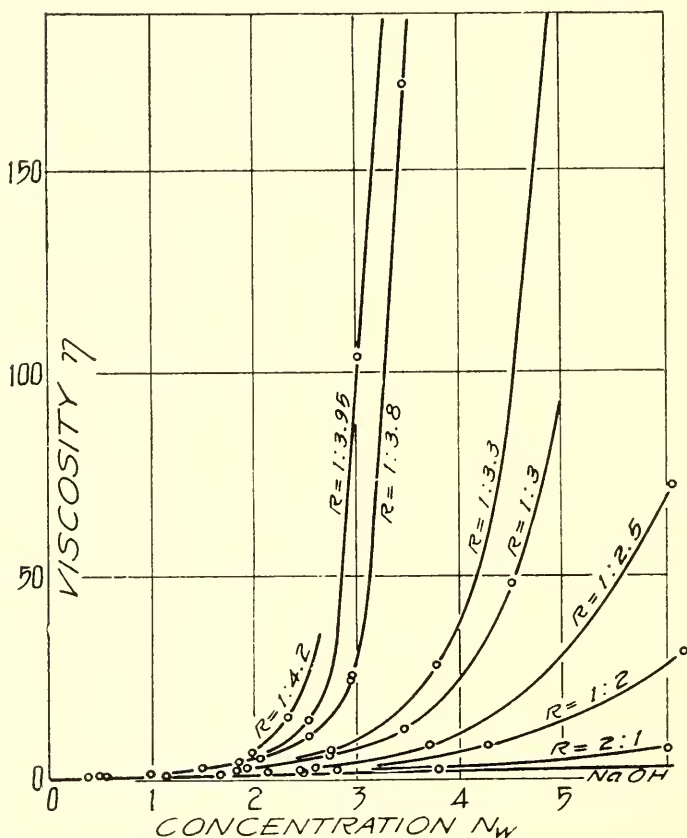
FIG. 63.—Results with Ostwald Viscometer.

Stericker [41] and confirmed by Dedrick [42] at higher concentrations was not shown.

The sharp rise of the curves to the left of the minimum does not affect adhesive silicates, for solutions in this range are too alkaline to be often chosen for such use. The shape of the curves, however, suggests that the disilicate at high concentrations has less internal resistance than either metasilicate or silicates with considerable amounts of colloidal silica.

[41] Stericker, *loc. cit.*
[42] Dedrick, Unpublished records of the Philadelphia Quartz Company.
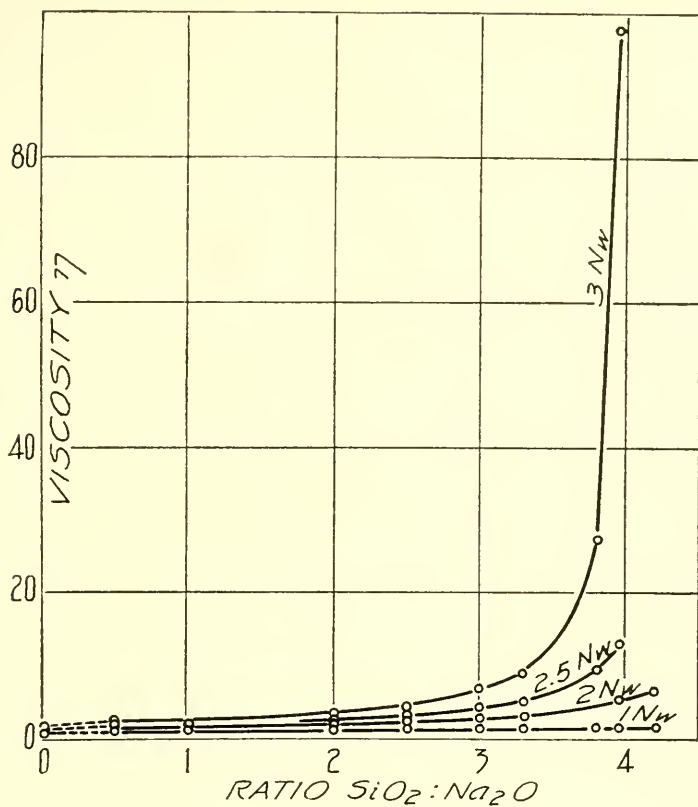
Fig. 64.—Ostwald Viscometer.
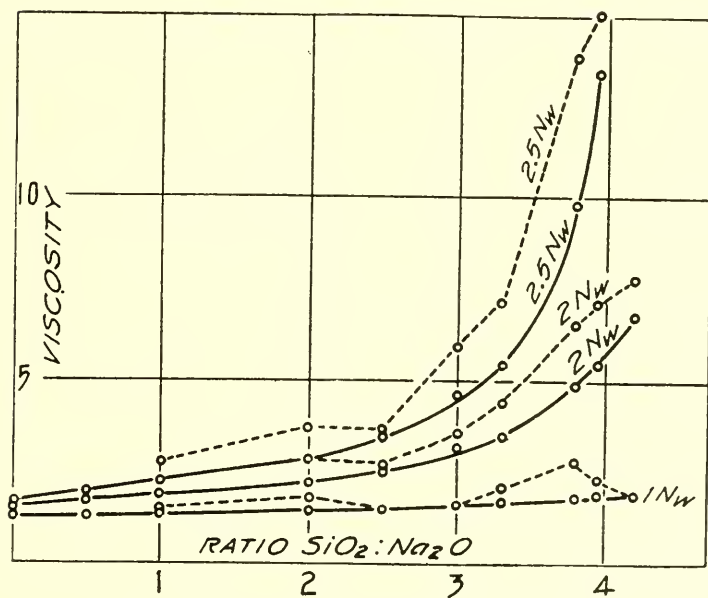
Fig. 65.—Change of Viscosity with Ratio.

TABLE 56. *Changes in Viscosity with Changes in Temperature.*

Temp. °C. Na₂O, 1.58SiO₂	Centipoises
Na_2O, $1.58SiO_2$	
10	307606
15	130986
20	61147
25	29519
30	14624
35	9391
40	5607
45	3900
50.5	2331
53.3	2158
60.6	1255
66.7	945
74.4	627
80.5	518

Temp. °C. Na_2O, $2SiO_2$	Centipoises
20.0	56016
21.1	37456
23.9	29803
26.7	18696
29.4	14342
32.2	10765
35.0	8122
37.8	6225
40.6	4779
43.3	3830
46.1	3115
48.9	2493
51.7	1902
54.4	1591
57.2	1441

Na_2O, $3.25SiO_2$. °Baumé 39.7	
1.7	509
4.4	384
7.2	331
10.0	287
12.8	242
15.6	216
18.3	192
20.0	176
21.1	174
23.9	167
26.7	142
29.4	129
32.2	116
35.0	105
37.8	92

Na_2O, $3.25SiO_2$. °Baumé 40.3	
1.7	758
4.4	565
7.2	440
10.0	449
12.8	311
15.6	268
18.3	230
20.0	216
21.1	210
23.9	182
26.7	173
29.4	167
32.2	132
35.0	129
37.8	109

Na_2O, $3.86SiO_2$. °Baumé 33.8	
10.0	798
12.8	400
15.6	255
18.3	187
20.0	165
21.1	161
23.9	119
26.7	98
29.0	83
32.2	72
35.0	61
37.8	51

Na_2O, $3.86SiO_2$. °Baumé 34.6	
12.8	922
15.6	479
18.3	290
20.0	231
26.7	132
29.0	121
32.2	110
35.0	96
37.8	83

Na_2O, $3.86SiO_2$. °Baumé 34.4	
12.8	2076
15.6	798
18.3	425
20.0	322
21.1	263
23.9	198
26.7	163
29.0	138
32.2	109
35.0	101
37.8	80

Temp. °C.	Centipoises	Temp. °C.	Centipoises
$Na_2O, 3.25SiO_2$. °Baumé 41		$Na_2O, 3.25SiO_2$. °Baumé 41.3	
4.4	857	4.4	1280
7.2	677	7.2	1052
10.0	434	10.0	789
12.8	423	12.8	681
15.6	397	15.6	542
18.3	353	18.3	468
20.0	331	20.0	430
21.1	314	21.1	390
23.9	269	23.9	343
26.7	237	26.7	298
29.4	216	29.4	269
32.2	190	32.2	235
35.0	176	35.0	210
37.8	165	37.8	191
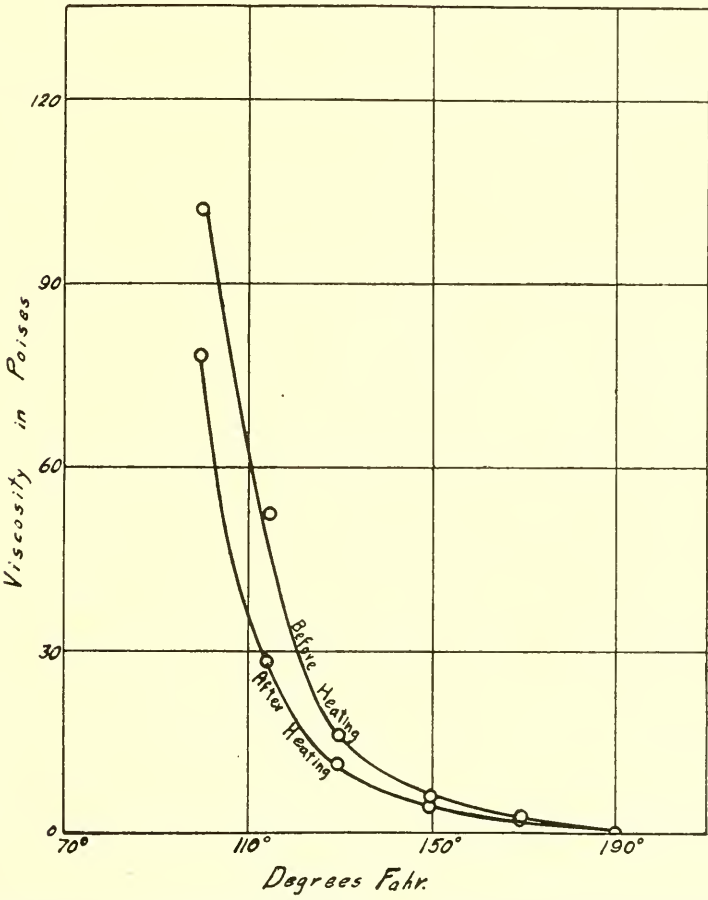
FIG. 66.—Changes in Viscosity of 60° Silicate Due to Heating under 70 Pounds. Pressure for Three Hours.

Changes Due to Heating. Viscosity is perhaps the most sensitive index of changes in equilibrium between the components of a soluble silicate in water. Carter [43] investigated the effect of heating 1 : 1.87 ratio

[43] Unpublished records of the Philadelphia Quartz Company.

solutions at temperatures above the boiling point of water and found that the change of viscosity with temperature was altered by this means.

TABLE 57. *Changes in Viscosity of Silicate of 1: 1.87 Ratio After Heating for 3 Hours at 70 Lbs.*

Degrees C.	Centipoises Before Heating	Centipoises After Heating
87.7–82.2	222.6	228.8
76.6–71.1	398.1	393.7
65.5	850.8	782.4
54.4	2052.0	1592.8
46.1	6567.0	3545.4
37.7	12648.0	9703.2

Effect of Salt Brine. Malcolmson [44] found that the viscosity of adhesive silicate solutions could be increased by mixing them with
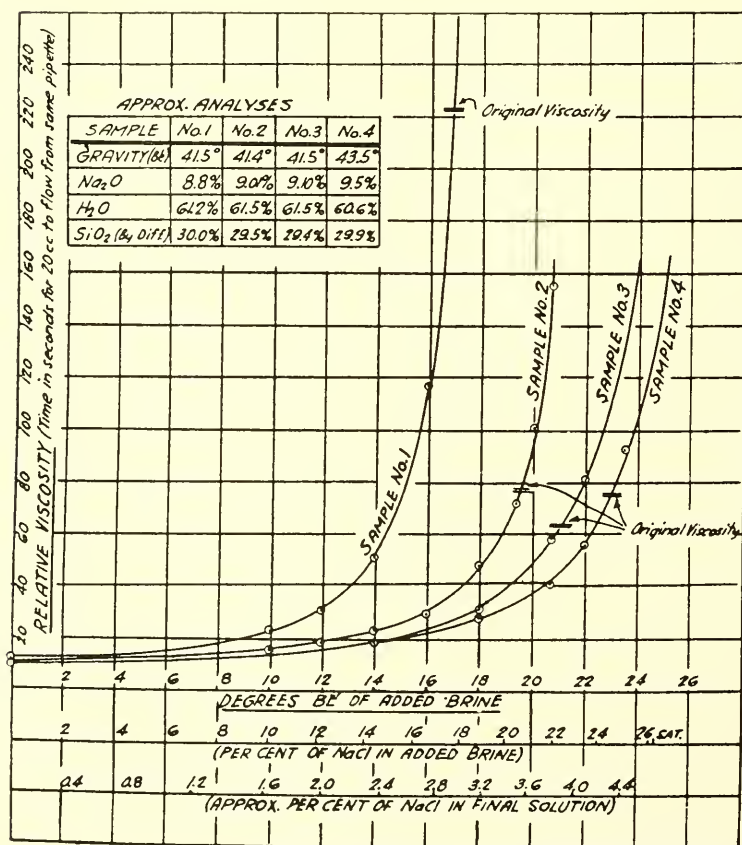
FIG. 67.—Effect on Viscosity of Silicate of Soda Produced by Addition of Various Brines.

[44] *Ind. Eng. Chem.,* **12,** 174-176 (1920).

sodium chloride brines. Thus a unit of adhesive could be increased in volume without loss of viscosity when it would spread over a larger area. The adhesive power, rate of drying and other essential qualities were not reduced below a point considered safe for making paper container board. By using a brine about 66 per cent saturated, the volume was increased 21 per cent without violating these conditions, but it should be pointed out that this was possible only because the adhesive strength of the silicate is so much greater than the paper that it can be much reduced and still have a good margin of safety.

The final viscosity was found to be dependent upon the concentration of the added brine, other factors being constant.

Stericker [45] discusses the probable mechanism of this increase in volume as follows:

"Sodium silicate solutions probably contain sodium, hydroxyl, silicate ions, undissociated silicates, and colloidal particles which consist largely of hydrated silica. Sodium chloride solutions contain sodium and chlorine ions and undissociated salt. Both contain, in common with all aqueous solutions, very small quantities of hydrogen and hydroxyl ions, due to the ionization of the water.

"When these solutions are mixed, the equilibrium between the various constituents is destroyed. Since at the concentration in question none of the salts present are completely dissociated, the solutions will be saturated with respect to sodium ions. There will be a tendency to repress these ions with the consequent formation of more of the undissociated salts and sodium hydroxide. The colloidal particles will

TABLE 58. *Variation in Hydrogen-Ion Concentration of Brine-Treated Silicate Solutions.*

NaCl in Brine	Relative Viscosity	E.m.f. in Volts	pH
Original Silicate Na_2O, $3.32SiO_2$; $38.9°$Baumé; Permanent Precipitate Formed.			
Orig. sil.	40.3	.898	9.65
16.3	28.4	.945	10.45
17.2	79.8	.944	10.44
20.4	436.	.875	9.25
Original Silicate Na_2O, $3.46SiO_2$; $39.8°$Baumé.			
Orig. sil.	68.0	.976	10.99
10.0	16.0	.960	10.71
13.7	22.4	.954	10.62
14.8	26.8	.950	10.54
17.3	47.2	.935	10.28
21.0	1180.	.951	10.56

[45] Stericker, *loc. cit.*

oppose this tendency by attracting the sodium ions to form adsorption compounds. The result is an excess of chlorine ions in the solution which give rise to more hydrogen ions. But since the concentration of hydrogen ions times that of hydroxyl ions is always a constant, some of the latter must disappear. Therefore, the hydroxyl ion concentration and the pH value fall until the silica particles are saturated. From this point on the change will be to depress the dissociation. At the same time the chloride may salt out the colloid, thereby increasing the hydroxyl ion concentration. From the results obtained it appears that this is what happens."

Tackiness. Lubricating oil and a sticky silicate solution may have internal resistances which make them flow at the same rate but there is a vast difference in quality. They may be alike in viscosity and yet different in what, for lack of a better term, we may call "tackiness", the ability to be drawn out into threads when two surfaces with a layer of the liquid between them are drawn apart. The silicate solutions vary all the way from an oily consistency which gives a lubricating effect to a stickiness which compares with that of sticky fly paper. This characteristic is obviously important for adhesives and it is easily and with a little experience accurately judged by rubbing a small portion of the liquid between thumb and finger and then drawing them apart. The stickiness of a silicate solution bears no direct relation to its adhesive strength nor yet to its final setting time.

Efforts to measure this property have been, up to this time, much less than satisfying. Mallock [46] considers that this property depends upon (1) resistance to change of volume and change of shape, (2) volume limits and shear limits, (3) surface tension. It is certain that a sticky liquid must have high cohesion and low surface tension. In general, sticky liquids easily wet surfaces to which they are applied. Looking at it from the angle of the colloidal silica, those liquids which have begun to form a structure will be the least tacky. A gel is an example of high viscosity and absence of the property under consideration.

The time factor must be taken into account in any effort to measure tack. Stericker [47] points out that either the instrument used for this purpose must be run at constant speed or the speed must be measured.

The U. S. Bureau of Standards developed an instrument for studying this property. It consists of a chemical balance from one beam

[46] *Proc. Roy. Soc. (London)*, **87**, ser. A, 466-478 (1912).
[47] "Annual Summary Report of Philadelphia Quartz Company's Industrial Fellowship," Mellon Institute, Pittsburgh, Pa. (1919-1920).

of which was suspended a conical bob. A wire loop between beam and bob served to prevent jerks and too rapid shearing. Weights applied to the opposite pan tended to withdraw the bob and the time required for the pointer to pass a certain number of scale divisions was measured.[48] Stericker obtained the following results by this method:

TABLE 59. *Attempt to Measure "Tack."*

Material	Centipoises	Time in Seconds with Weight of:			
		17.4 g.	17.6 g.	18.0 g.	18.02 g.
1 Lubricating oil	124.5	Too rapid to read		....	....
2 $Na_2O, 2.1SiO_2$ diluted	124.5	11	....	....	....
3 Viscous oil	2704.4	21.5	2.1	....	....
4 $Na_2O, 2.1SiO_2$ diluted	2548.9	44.4	11.3	4.5	2.6
5 Dextrin	....	....	....	137.	69.
6 $Na_2O, 2.1SiO_2$	124.5	....	....	171.	....
7 $Na_2O, 1.24SiO_2$	....	....	....	3.8	....
8 $Na_2O, 2.84SiO_2$	969.0	....	6.3	1.2	....
9 $Na_2O, 3.41SiO_2$	522.0	....	1.5	1.0	....
10 $Na_2O, 3.47SiO_2$	247.5	....	1.3	0.7	....
11 $Na_2O, 3.32SiO_2$	167.2	....	0.6	0.6	....
12 $Na_2O, 3.92SiO_2$	....	....	....	1723.	....
13 $Na_2O, 3.47SiO_2$ (control) ..	247.5	....	0.8	0.7	....
14 Na_2O + sodium acetate	281.7	....	1.0	0.7	....
15 Na_2O + urea	261.2	....	1.0	0.8	....
16 $Na_2O, 3.92SiO_2$ + 20% H_2O..	....	1.4	0.6	0.7	....

The difference between a tacky liquid and one of like viscosity which is not tacky is brought out in the comparison of 3 and 4 but tackiness can be developed only in viscous liquids. Thus the high value of number 12 is somewhat misleading for though at the speed of the experiment $Na_2O, 3.92SiO_2$ at the high viscosity appears tacky, yet the fact that at higher speeds the threads of this liquid break off short while those of $Na_2O, 2.1SiO_2$ solutions of the same viscosity do not is not shown. It might be by extending the study to faster movement of the bob. This method is the best yet devised but must be much further studied to be of much use. It gives consistent results in skilful hands but would have to be simplified to be of value for controlling adhesive silicates. Tackiness decreases as the silica ratio increases and it declines with temperature, but the work has not been carried far enough to say whether the latter is due to fall of viscosity with rising temperature.

The method proposed by Bonney[49] is more convenient especially in mixtures of silicate with inert material but has not been worked out for very sticky viscous substances. He plots time against distance

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[48] Basseches, J. L., Bur. of Standards, personal communication.
[49] Bonney, Robert D., *Catalyst,* 8, No. 3, 8 (1923).
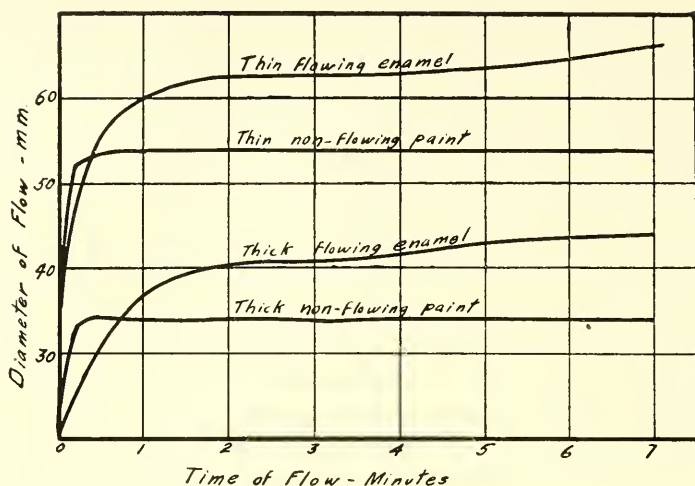
Fig. 68.—Spreading Characteristics of Paints.

traveled while a large drop of the substance under test flattens out on a smooth glass plate. Characteristic forms of curves for tacky and "short" adhesives are thus secured.

METHODS OF ANALYSIS.

GLASS.

If the sample be a solid glass, it is most convenient to bring it into solution by slow hydration with steam, thus avoiding the uncertainties which arise from adding alkali carbonates to make an easily soluble fusion. Silica, sodium oxide, and impurities may then be determined directly in the same sample and with a great saving of time. Finely ground glasses may be weighed out and subjected to open steam until they are hydrated sufficiently to dissolve completely in hot water. This method is applicable to ratios up to and including $Na_2O, 3.3SiO_2$, a half gram sample of which can be hydrated on a water bath in about $2\frac{1}{2}$ hours. No water should be put on the silicate; hydration takes place best from the steam direct. A shallow dish such as an inverted porcelain crucible lid supported on a triangle and covered with a round bottomed glass dish is a suitable arrangement. A small pressure cooker or autoclave capable of quickly raising fifteen pounds steam pressure will shorten the dissolving time to about an hour.

DETERMINATION OF SODIUM OXIDE.

When solution is complete, the whole container should be placed in about 75 cc. of distilled water, stirred with a glass rod, and one drop of standard methyl orange solution added, as soon as the solution is

cold. The silicate should be entirely dissolved without leaving any grit. If there is grit, it means that the sample has not been ground finely enough or that it has not been on the steam bath long enough. Titration is carried out with standard hydrochloric acid.

Sodium oxide is determined, in the liquid grades, by weighing from 0.5 to 2 grams of the silicate in a small porcelain crucible, covered with a watch glass. Care must be taken to avoid any surface skin which may have formed on the sample. The silicate and crucible are put in a beaker of water,—hot water in the case of the heavy silicate solutions. When the sample has cooled to room temperature it is titrated as above.

Sodium oxide is best determined by titration with $N/5$ hydrochloric acid and methyl orange, which gives a much sharper end point in silicate than in carbonate solutions. Phenolphthalein always gives low results. The error is greatest with the solutions of high silica ratio. Stericker [50] found the fractional amounts of the total titratable with this indicator.

TABLE 60. *Errors from Titration with Phenolphthalein.*

Mols SiO_2 per Mol Na_2O	Per Cent Total Na_2O Found with Phenolphthalein
1.69	95.3
2.06	92.5
2.40	93.0
2.44	91.7
3.36	87.1
3.90	85.1

This may be due to adsorption of sodium oxide on colloidal silica or to the formation of acid silicates. The end point is difficult to fix and this indicator should not be used. Methyl red and brom-phenol blue are satisfactory, but phenol red, attractive on account of its resistance to hydrogen peroxide, only gives part of the total sodium oxide in silicate solutions.

DETERMINATION OF SILICA.

The silicate solution is evaporated twice to complete dryness with hydrochloric acid and the silica is washed and ignited to constant weight. As a check the silica is volatilized with hydrofluoric acid and the residue weighed. It should be very small. Hillebrand's technic [51] is the

[50] "Annual Summary Report of Philadelphia Quartz Company's Industrial Fellowship," Mellon Institute, Pittsburgh, Pa. (Sept., 1922).
[51] Hillebrand, "Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey, Bull.* **700** (1919).

best for precise analysis in the presence of other silicates than those of the alkalies, but the procedure can be somewhat shortened for soluble silicates.

Harman [52] discusses sources of error in determining silica as follows:

"Incomplete removal from solution owing to an insufficient number of evaporations to dryness. Two are sufficient in the case of a simple silicate such as used here, provided each is a very complete evaporation to dryness.

"Failure to remove particles of silica from the evaporating dish. This error may be quite large but can easily be avoided by wiping the dish with a piece of moist filter paper which is then added to the silica to be ignited.

"Improper ignition. The error here may vitiate the whole experiment. It is best to begin the ignition with a bunsen flame about the size of an ordinary match flame, gradually increasing it so that the paper distils as a tar on to the crucible lid and finally disappears. If at any time the escaping gases should catch fire, the experiment is quite worthless, owing to the fine particles of silica being carried away by the draught. Finally ignite in a Meker burner till constant weight is obtained—usually half to one hour. The silica residues were always snow white.

"By using these and the usual precautions, duplicate analyses for SiO_2 agreed within 0.01 per cent."

DETERMINATION OF WATER.

Water may be determined in the solid glass or powders by simple ignition to constant weight in a platinum crucible over a Meker or equivalent burner.

Determination of moisture in the liquid grades, however, requires considerably more care. Precaution must be taken to prevent the loss of silicate. This is best done by carrying out the initial heating below the boiling point of water. When most of the water has thus been driven off, the temperature is gradually raised. If the temperature is increased too rapidly, the silicate will sputter and puff out of the container. The last traces of moisture are only removed by ignition. Fusion with additional sodium carbonate gives a mass which can be more readily removed from a platinum crucible after such a determination.

[52] Harman, R. W., *J. Phys. Chem.*, **30**, 362 (1926).

Ordway[53] proposed a method which permits more rapid heating by preventing the intumescence. He poured the silicate solution on a weighed portion, preferably about two grams, of freshly ignited anhydrous calcium sulfate.

COMPOSITION.

Although the differences in physical properties of commercial silicate solutions are very wide, ranging from liquids which are almost
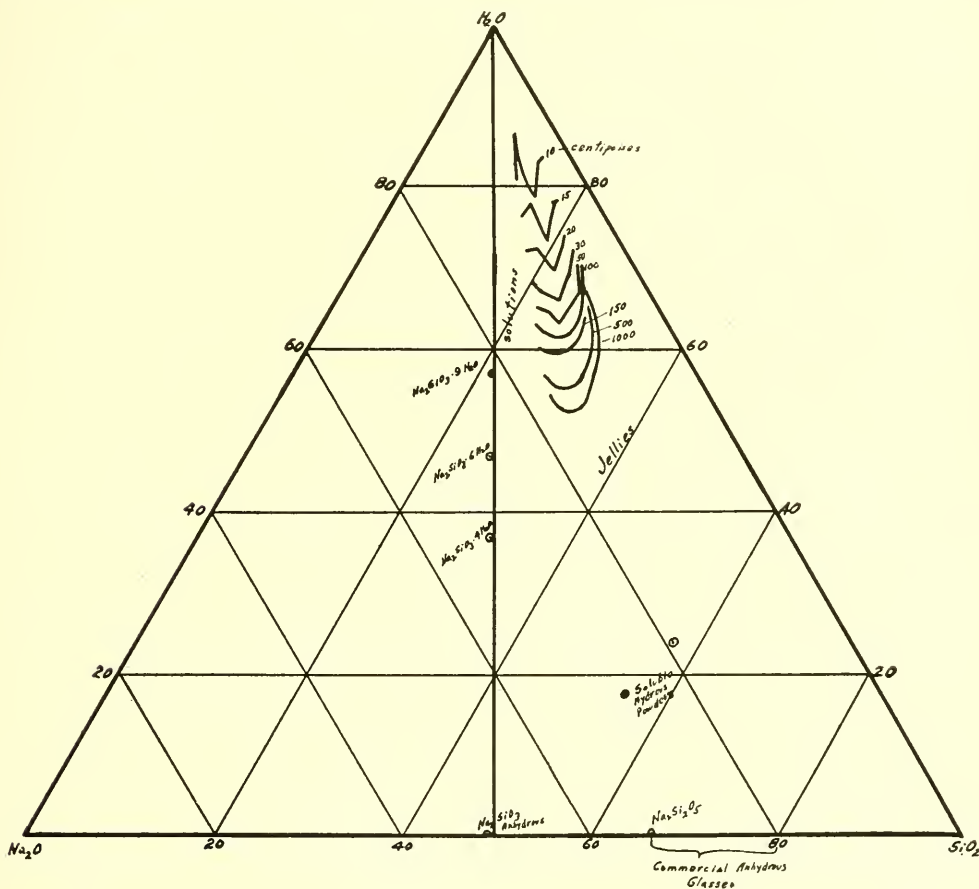
FIG. 69.—Commercial Silicates in Relation to the System Na_2O–SiO_2–H_2O.

jellies to liquids comparable in stickiness with the thickest molasses, yet if we consider the possible combinations of the three components from which these solutions are made they all fall within a comparatively narrow range.

This point is best brought out in the triaxial diagram. Along the base line we may represent anhydrous mixtures of Na_2O and SiO_2 in any proportion. These are the glasses produced by fusion. The

[53] *Am. J. Sci.*, ser. 2, **33**, 27-36 (1862).

points on the line fix the important question of ratio which must be grasped in order to apply intelligently any kind of silicate of soda in industry. Having fixed a point on the base line, let us take for example that representing $Na_2O, 3.3SiO_2$, neutral glass of commerce. We may draw a line to the apex of the triangle designated water. Along this line will fall all mixtures of this ratio and water. The most familiar solution, often referred to as commercial 40°, falls at the point where 62 per cent water is shown. If we thus locate all the grades which are industrially significant, we shall find that they fall within an area which includes the lower group of iso-viscosity lines and some points representing higher concentrations. It is convenient to transport silicate solutions at the highest concentrations which are consistent with handling them as liquids. All these fall within a comparatively small section of the diagram.

TABLE 61. *Typical Analyses of Commercial Grades.*

Constituents	$Na_2O, 3.97SiO_2$	$Na_2O, 3.31SiO_2$	$Na_2O, 2.74SiO_2$	$Na_2O, 2.05SiO_2$	$Na_2O, 1.61SiO_2$
Sodium oxide, Na_2O.....	6.34	9.12	13.80	18.07	20.75
Silica, SiO_2	24.47	29.37	33.33	35.64	34.84
Iron oxide, Fe_2O_3........	0.025	0.024	0.02	0.03	0.02
Alumina, Al_2O_3	0.092	0.087	0.17	0.13	0.17
Titania, TiO_2	0.006	Trace	0.002	0.01	0.007
Lime, CaO	0.013	0.059	0.02	0.03	0.04
Magnesium, MgO	0.044	0.024	0.006	0.02	0.01

English Neutral Silicate, $Na_2O, 3.19SiO_2$, 39.8°Baumé		English Silicate, $Na_2O, 3.02SiO_2$, 45°Baumé	
Na_2O	8.76	Na_2O	10.42
SiO_2	27.21	SiO_2	30.62
Fe_2O_3	0.006	Fe_2O_3	0.01
Al_2O_3	0.08	Al_2O_3	0.09
CaO	0.07	CaO	0.05
MgO	0.04	MgO	0.06

The difficulty and expense of preparing easily soluble forms of silicate, on the one hand, and the technical control necessary to make solutions of the required exactness, on the other hand, have resulted in the practice of bringing the principal tonnage of soluble silicates on the market in solution, and this in turn, has resulted in a tendency to locate manufacturing plants in the centers of consumption rather than, as in many industries, with primary regard to raw materials, water, and fuel.

The concentration at which any of these solutions can be marketed

depends primarily upon viscosity. The named areas on the triaxial diagram indicate in an approximate way the physical character of the three components outside the range of commercial products. To make
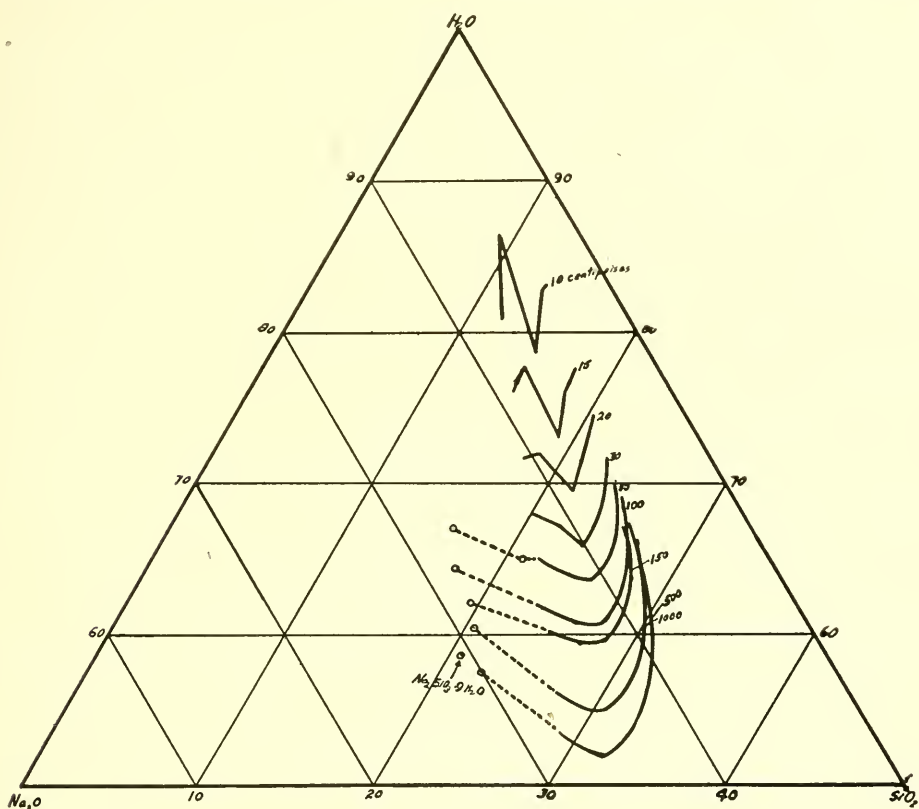
FIG. 70.—Iso-Viscosity Curves of Silicate Solutions.

this relationship clearer iso-viscosity lines have been indicated upon an enlarged section of the triaxial diagram, the data being the same as those presented during the discussion of viscosity.

CONTAINERS.

TRANSPORTATION AND STORAGE.

Products of fusion in lump form are stored and transported either in bulk or in jute sacks. When powdered, they take up enough moisture from the air to stick together and to a greater or less degree absorb CO_2. They should, therefore, be kept in tight containers, preferably of metal. Considerable misapprehension exists about the ability of asphalt coatings or even rubber lined sacks to prevent absorption of moisture. It is a fact readily verified that containers sufficiently water-tight to be used for the transport of dry calcium chloride will not

prevent the powdered forms of silicate of soda from caking. This statement does not necessarily hold for mixtures of silicate with other substances. Wooden barrels are used for containing silicate powders for a short time, but caking invariably takes place on long storage unless the surrounding atmosphere is exceptionally dry. Solutions are also shipped in wood through which moisture continually evaporates with resulting concentration. This is almost negligible for commercial 60° $Na_2O, 2SiO_2$ containing 46 per cent water, but for 40° $Na_2O, 3.3SiO_2$ it is a serious disadvantage, causing a thickening of the liquid to practically solid consistency in a few months. A solution, the viscosity of which is in the steep part of the viscosity-concentration curve, may change its character completely in a short time in wooden packages. Test kegs containing 47° Baumé adhesive silicate $Na_2O, 3.11SiO_2$ and placed in a warm room showed the following changes:

Time	Centipoises
At the start.......	1280.00
After 1 day	1317.32
After 2 days.....	1404.40
After 4 days......................	1591.00
After 7 days	1902.00

The changes which may occur in silicate stored in glass bottles are illustrated by the picture of two bottles filled with the same silicate to approximately the same level at the same time. They were corked and sealed with wax, which in one case was broken by accident. The composition of the original solution was:

SiO_2	20.78
Na_2O	5.13
Al_2O_3	0.036
Fe_2O_3	0.007
H_2O	74.0
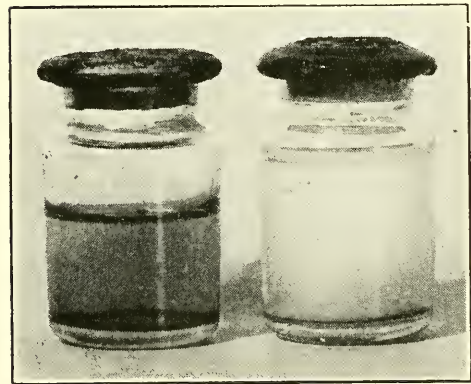
Fig. 71.—Silicate Samples Stored in Glass, Showing Effect of Evaporation through Cork.

At the end of a year the sample with the broken seal had evaporated and formed a clear, transparent solid. The other had kept its original volume but was a turbid gel which, however, became clear on warming to 40°C. and resumed its turbid appearance gradually, beginning some time after it had cooled. This cycle could be repeated, but gradually the gel was disrupted under this treatment by

syneresis. Other samples of the same solution kept in closed iron drums were apparently unchanged. Metal drums, tanks, and tank cars are therefore to be preferred. Galvanized metal should not be used because during storage it is possible for sufficient reaction between zinc and alkali to take place to cause evolution of hydrogen and bursting of the package. If a galvanized container partly full of silicate were subject to alternating heating and cooling as from day to night water might condense upon the walls of the container and flow down, forming a film of silicate sufficiently dilute to be reactive. Storage tanks of wood, iron, and concrete are in successful use, the last on account of convenience and economy in construction are coming increasingly into vogue.
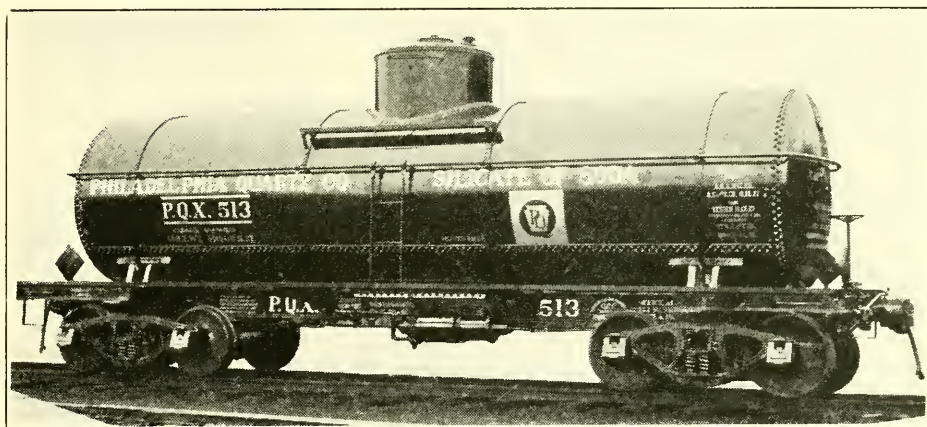
Fig. 72.—Tank Car for Silicate.

Cans of tin or tin plate are extensively used for silicate solutions in small quantities. $Na_2O,3SiO_2$ and more silicious silicates at concentrations above 38 per cent leave the metal perfectly bright in most cases. $Na_2O,2SiO_2$, sometimes sold for egg preserving, though in the judgment of the author, inappropriately so, will usually cause some solution of the metal at concentrations below 55 per cent. The crystalline structure of the coating appears as a result of the etching, although the amount of metal removed is very small and for practical purposes negligible. Solutions more alkaline than $Na_2O,2SiO_2$ and sufficiently dilute to be fluid attack solder and sometimes cause leakage.

PUMPS.

Adhesive silicate solutions are moved about in quantity through ordinary equipment for handling liquids, rotary pumps being used on most installations and centrifugal or plunger pumps for larger quan-

tities with no other precaution than to keep stuffing boxes tight by saturating with mineral oil and graphite free from saponifiable material and, where necessary, applying a water gland or similar stream of water to the point at which the shaft emerges from the stuffing box. This effectually prevents hardening of silicate and the abrasion which would result if it were allowed to dry. Tank cars are emptied either
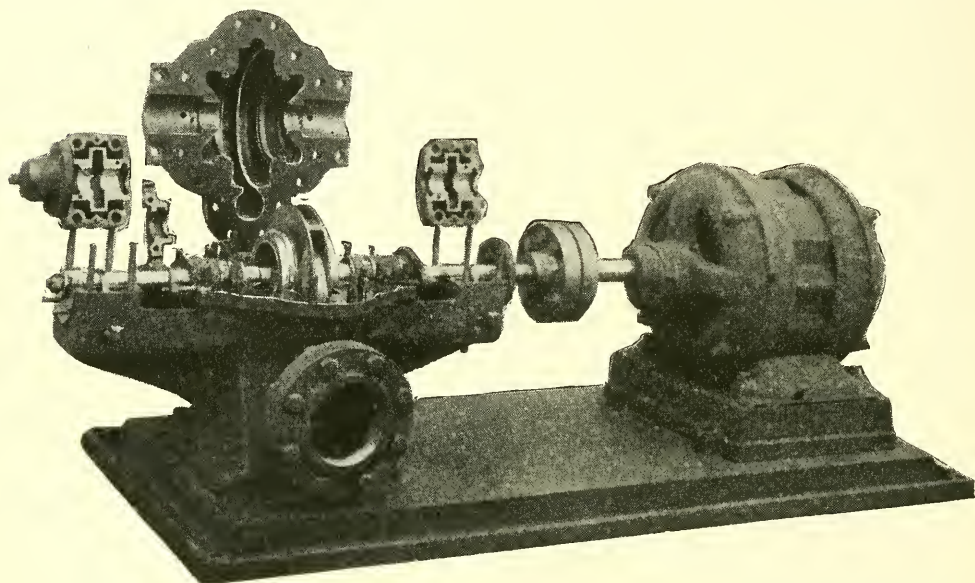
Fig. 73.—Centrifugal Pump of a Type Satisfactory for Silicate Solutions.

by pumping out the liquid or by introducing air at the top to expel it. Tank cars used in cold climates must be equipped with heating coils to permit thawing solutions which freeze in transit. It has been experimentally determined that silicate in a tank car can be thawed by building a fire under it but this does not inure to the satisfaction of the owner. Wooden cradle blocks and paint are combustible, and even metal parts are subject to damage when abused in this way.

Chapter VII.

Silicate Cements.

Industry has frequent need for substances to make joints between metals, refractories, fibrous sheets, and all sorts of structural material. In addition to closing joints which would otherwise be imperfect, it is often necessary to improve the service of the principal material of construction by means of a coating which will modify the surface and fit it for some special type of exposure.

Cements have been made in a great many ways and thousands of formulas are to be found in the literature. Some of them are illogical, many are unnecessarily complicated or costly, and others are in successful use as result of custom rather than because a systematic study has shown them to be best fitted for their work.

Soluble silicates are at least mentioned in every compendium of formulas for cements. They have found very numerous uses along this line, but the general criticism of the literature, that too much is left to the imagination of the reader, is warranted; it is too often assumed that he will know which silicate to choose, at what concentration to use it, and other details which may not occur even to experienced workers.

Both the conditions which a cement may be required to meet and the character of ingredients are so various that some experimental work is inevitable. It is the purpose of this chapter to indicate the nature of the variables most likely to be met, and thus to help that person who wishes to formulate a mixture for a given use, rather than to present a set of recipes for use without experimental preliminaries.

Cut-and-try methods are still essential because our knowledge of the physical and chemical processes on which these mixtures depend is not yet sufficiently complete or exact to permit a precise forecast of the behavior of any mixture without a basis of experiment.

Definition of Cements and Adhesives.

The line between cements and adhesives is not sharply drawn, but it is convenient to divide between fluids which are applied as thin

films to unite surfaces nearly in contact and the more viscous masses which, though they may be sticky and exert adhesive properties, are yet expected to occupy more space than adhesives proper. In many instances, the primary function of the latter group is to close openings or to form one of the elements of a structure such that they must be used in thick masses. We shall call them cements.

Any adhesive liquid may be mixed with inert solid matter, more or less finely divided, to form plastic bodies which occupy space or serve to resist, in some degree, tensile or compressive stress. Silicates of soda have been widely used for diverse purposes in combination with many substances which act in the rôle of fillers.

Classification of Silicate Cements.

Cements in which soluble silicates are of use may be divided into three groups:

1. Those which set primarily by loss of moisture from the silicate solution.

2. Those which depend upon a reaction with the silicate to become firm.

3. Those in which silicate is used to modify the properties of other cements.

The materials which are of use as accessories to modify the physical character of silicate cements, beyond the variations obtainable by using silicate solutions of diverse concentration and ratio, group into substances which alter the liquid phase and those which affect the solid part of the cement mixture.

Cements Which Set Primarily by Loss of Moisture.

General Properties.

The properties of such mixtures will depend upon the character of silicate used, that is, the ratio of base to silica, upon its concentration, and upon the kind of filler and its physical state. From the same silicate solution with the same filler we may make mixtures as different as paint and putty. Without changing the concentration of the silicate, the state of division of the pigment will alter the plasticity of the mass and its final strength. Diluting the silicate solution enables it to carry more inert mineral matter, and beyond an optimum point reduces final strength. Thus a mixture which might dry to a

glossy surface with one concentration of silicate would yield a flat surface with greater dilution and finally a soft mass easily broken down. Assuming an inert pigment, the various ratios of base to silica give the whole range between quick-drying substances which seem more
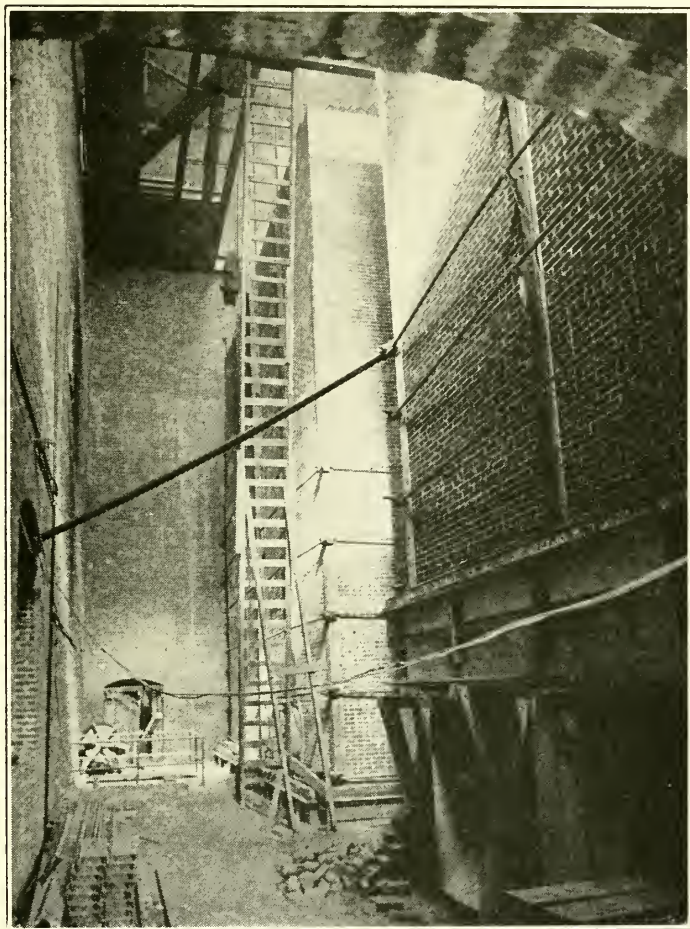
FIG. 74.—Sulfuric Acid Towers Laid with Silicate Cement.

like lubricants than anything with bonding strength, to the very sticky solutions which thread, like strong solutions of animal glue, and set very slowly.

Endless variants can be introduced by using solid substances capable of reaction with the silicates and by adding materials such as oils, soaps, glycerin, fibers, et cetera, to modify the character of the final mass. A great number of specific formulas have been offered.[1, 2] It

[1] Breuer, Carl, "Kitte und Kiebstoffe," Leipzig, 1922, 189-198.
[2] Hacker, Willy, "Handbuch der Kitte und Klebemittel," Meissen, 1920, 153-156.

is obvious that this process could be continued ad infinitum, but it will be of greater service to show some of the characteristics of these mixtures and allow specific formulas to take a secondary place.   They
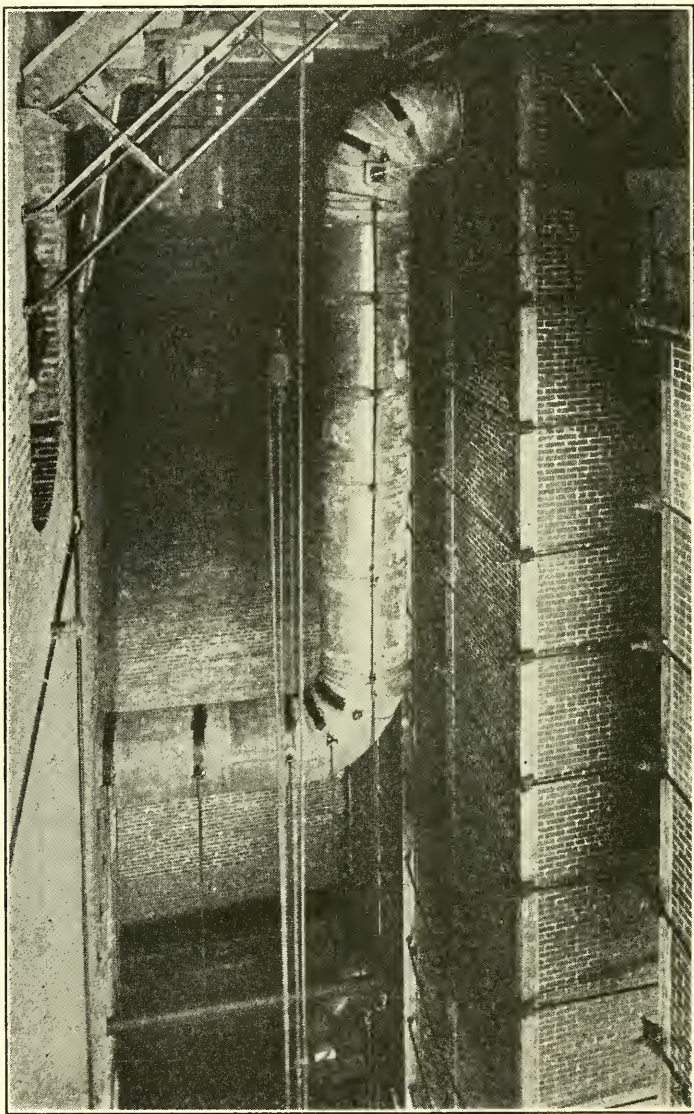
FIG. 75.—Acid Towers Laid with Silicate Cement.

are easily worked out when the behavior of the raw materials is understood.

FILLERS.

Silica as the Filler.   The simplest silicate cement is one composed of a silicate solution made up to a pasty or putty-like consistency with

some form of silica which may be regarded as an inert substance with respect to silicate solutions of the composition $Na_2O,3SiO_2$, or those containing more silica at ordinary temperatures.[3] A cement of this sort is used in the construction of acid-proof masonry. Its character may obviously be varied by the ratio of the silicate used, by the amount of silicate dissolved in the water, and by the state of subdivision of the inert material. The cement is used to lay between bricks of a
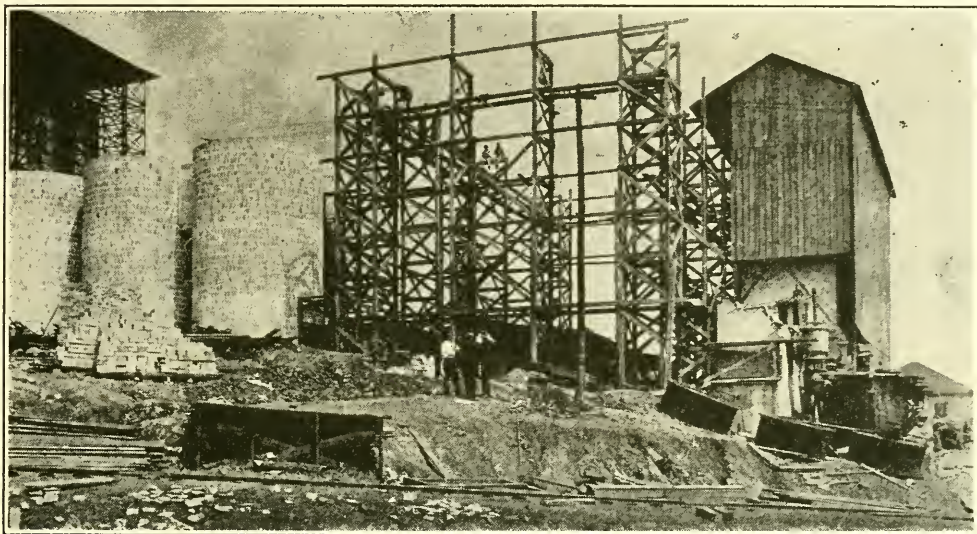
Fig. 76.—Silicate Cement in Acid-Proof Construction.

dense sort which will be comparatively impermeable to acid. It will be mixed immediately before use and it is desirable that it should set as promptly as is consistent with long service. These conditions point to the selection of a high ratio silicate because we know from the viscosity-concentration curves that this type of silicate passes from a liquid to a solid condition with the least loss of moisture. Let us assume, then, that $Na_2O, 3.9SiO_2$ is to be used. This choice would not be appropriate if the cement were required to remain soft on long storage because the wet mixture hardens too easily. Further, as acid resistance is sought, we want to produce a mass which will finally consist as nearly as possible of pure silica with a minimum of porosity. On this account the smallest possible amount of sodium oxide is wanted.

Having selected the right ratio, the next point is to decide at what concentration it should be used. If we mix quartz into a thick gelatinous silicate solution, a comparatively small amount of filler can be used, as the mixture would become too dry and thick to work prop-

[3] For example, Winship, William, U. S. Pat. 1,587,057 (June 1, 1926).
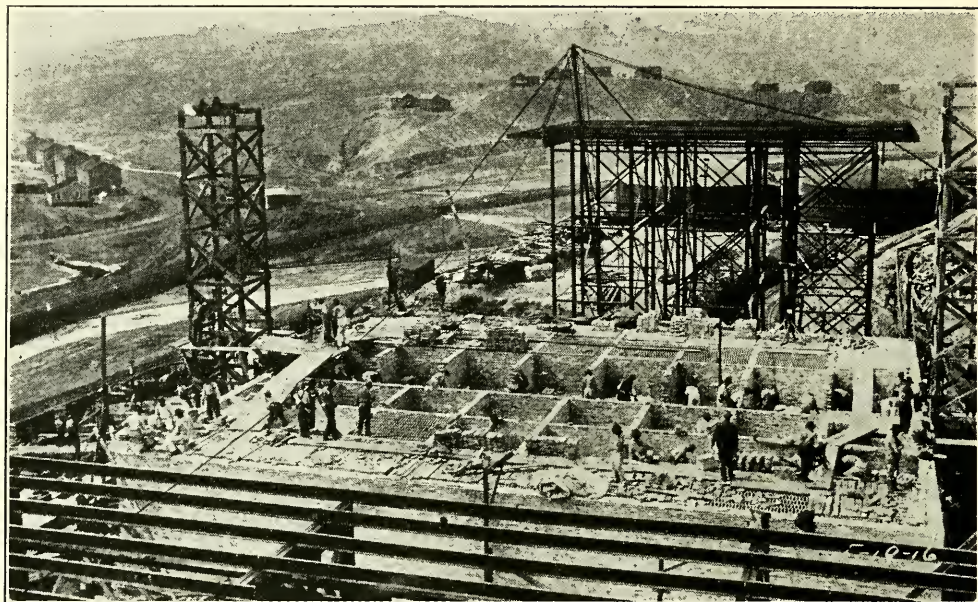
Fig. 77.—Silicate Cement in Acid-Proof Construction.
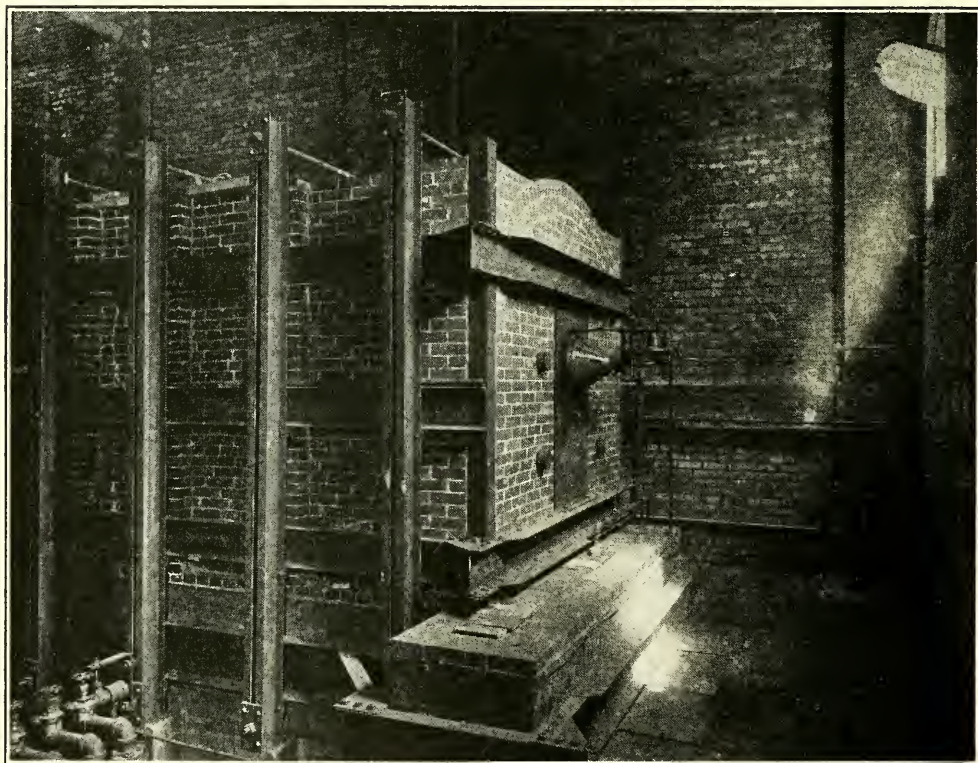
Fig. 78.—Silicate Cement in an Oil-Fired Acid Concentrator for H_2SO_4.

erly under a trowel or to form a proper bond. Shrinkage will also be troublesome. If too much water is present a much larger amount of silica can be used, but the silicate will then be spread over too large a surface and the air-dry cement will be weak. Experience indicates that a specific gravity of 1.30 is about right.

Effect of Grain Size. Another factor of importance is the degree of subdivision of the silica filler. A series of experiments in which standard briquets, such as are used for tensile testing of Portland cement, showed that air-dried silicate cement containing 50 parts by weight of silicate solution and 110 parts by weight of 100 mesh silica average 788 pounds per square inch tensile strength. Mixtures of grain sizes were studied in order to make a body of maximum density and it was found that by making the filler of equal parts by weight of silica passing a screen of 100 meshes to the inch (Tyler standard)[4] and a grade between 20 and 40 meshes, the tensile test of air-dry briquets rose above 1500 pounds per square inch. By the interlocking of sharp angular grains of various sizes a much stronger body was produced than that obtainable from either size by itself.

Although the strength of such cements is obviously dependent upon the binding properties of the silicate, it does not follow that the optimum amount of silicate is the maximum consistent with good working properties of the soft mixture, as illustrated by the following experiment. Crushed silica rock of the following screen analysis was used:

Mesh	Per Cent
14–20	3.6
on 28	3.6
" 35	7.1
" 48	12.5
" 65	16.0
" 100	17.8
" 200	17.8
through 200	21.6
	100.0

Silicate of the composition $Na_2O, 3.3SiO_2$ at a density of 1.39 gave the following results:

Parts of Silica	Parts of Silicate	Tensile Strength of Briquets Dried to Constant Wt. at 49°C.
100	33.1	612
	31.3	556
	29.5	706
	27.8	1472
	26.0	1603

[4] W. S. Tyler Company booklet, Cleveland, Ohio.

Another combination of grain sizes or a different filler might require different amounts or concentrations of silicate to give the best results, but the illustration will suffice to point out that the proportioning of ingredients is a matter of prime importance to be worked out for each kind and size of inert filler.

Using a calcined fire clay, the following strengths were obtained with the same silicate on various sizes.

TABLE 62. *Tensile Strength Figures.*

Mesh	Tensile Strength
4– 8	331
8– 10	529
10– 14	558
14– 20	584
20– 28	479
28– 48	492
48– 65	596
65–100	556
100–200	495
through 200	295

From this it may be seen that with the exception of the coarsest and the finest fractions, bodies of similar strength were obtained.   The

TABLE 63. *Tensile Strength Figures.*

Screen Analysis		Parts Silicate Solution	Tensile Strength
10– 14	39.1		
14– 20	1.1		
20– 28	2.2		
28– 48	3.9	33.2	754
48– 65	2.2		
65–100	8.0		
100–200	20.4		
through 200	23.1		
8– 10	51.1		
10– 14	1.2		
14– 20	2.1		
20– 28	1.5		
28– 48	.9	33.5	923
48– 65	10.3		
65–100	3.6		
100–200	12.4		
through 200	16.9		
28– 48	46.5		
48– 65	3.5		
65–100	7.4	33.1	1072
100–200	13.2		
through 200	29.4		
28– 48	48.0		
65–100	9.3	37.4	1154
100–200	24.4		
through 200	18.3		

effect of mixing the sizes without changing the quality of silicate or inert filler is seen from the following, which also indicates the change in the amount of the same silicate required to give similar consistency.

Abrasives.

Ransome [5] appears to have been the first to devise an artificial stone with a sodium silicate binder. Hart made excellent grinding wheels by employing silicate as the binder, in place of a linseed oil, which was commonly used.

Fig. 79.—Forming a Silicate Grinding Wheel.

Wire Web Wheel. In an effort to protect the worker in case of breakage while grinding, Hart [6] devised an abrasive wheel containing a wire web. This was widely used, and for fifteen years was the best grinding wheel on the American market, and saved a great many accidents before modern protective shields and grinding methods had been developed. The silicate made possible a low-temperature bond which

[5] Ransome, Frederick, Brit. Pat. 505 (Feb. 27, 1861); Report of the British Association for the Advancement of Science, **42**, 248-249 (1872); *J. Soc. Arts,* **7**, 593-595 (1859).
[6] Hart, U. S. Pat. 201,778 (March 26, 1878).

allowed the insertion of a strong brass wire in the stone. This process is essentially the making of a silicate cement which sets by drying, although small amounts of reacting materials are usually added to abrasive wheel mixtures. The reactions have not been fully studied and are not adequately understood. Pulpstones and refractory masses are made from sand or clay and silicate solutions at temperatures of incipient fusion.[7, 8]
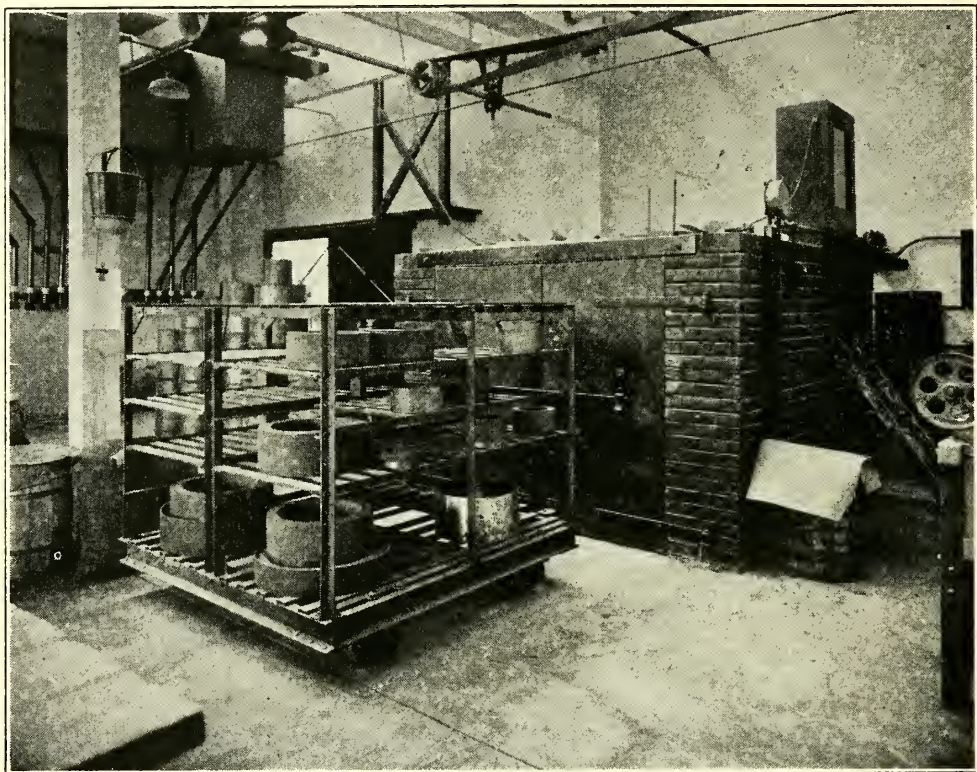
Fig. 80.—Silicate Wheels Ready to Be Baked.

Method for Making Abrasive Wheels.[9, 10] A typical formula for making a grinding wheel by the silicate process might call for 100 pounds of 20 mesh aluminous abrasive grain and 12.5 pounds of a finely powdered clay or silica. The binder consists of 12.5 pounds of 59.1° (commonly called 60°) Baumé silicate of soda, specific gravity 1.688 and composition $Na_2O,2SiO_2$. This is a very viscous solution, about 79.5 poises, and it does not at first appear possible to work the ingredients into a uniform condition. A slow moving power mixer

[7] See also Barron, W. S. and G. S., Brit. Pat. 123,377 (Feb. 18, 1919).
[8] Greenwood, W. W., *Paper*, **35**, No. 17, 12 (1925).
[9] Anon., *Abrasive Ind.*, **6**, No. 6, 191 (1925).
[10] Iding, Mathew, and Wm. A. Nimtz, U. S. Pat. 1,635,675 (July 12, 1927).

is used, the abrasive is put in, and the powdered clay weighed and spread out on the weighing vessel. The silicate is then weighed on to the powder which prevents it from sticking to the container, and silicate and powder are slid together into the mixer. Without some such device, it is difficult to weigh with accuracy sufficient to control the grade of hardness desired in the wheel. After thorough mixing, each abrasive grain is covered with a sticky layer of silicate; and the mass is in condition to be tamped or pressed into molds, a matter requiring a considerable degree of skill to produce a uniform texture.

Fig. 81.—Silicate-Bonded Abrasive Wheels.

A process of air-drying at temperatures below 100°C. follows until the mass has set up sufficiently rigid to avoid danger of distortion, and the final step is a baking process at 180° to 260°C. until the wheel has thoroughly hardened. This is the most convenient method of making large grinding wheels and has the advantage that the entire operation can be carried through quickly. A 12″ × 2″ wheel can be mixed, dried, baked, and put into service in 12 hours, though longer time is needed for large wheels. In any case, the time is much less than that needed to form a ceramic bond.

Wheels for grinding cutlery and for operations requiring a smooth finish are generally made with a silicate bond. Many wheels for glass cutting are also made by this process. As these wheels are required to run wet, the question of adequate water-resistance is important. A small

quantity of zinc oxide is usually added to the mixture for such wheels
and it probably reacts to form an insoluble zinc silicate, but the amount
used is less than the equivalent of the Na_2O in the silicate, and a con-
siderable degree of water-resistance is secured without it.   Perhaps
when clay is used there is some formation of sodium aluminum sili-
cate, such as analcite and feldspar; but if the subject has been investi-
gated the results have not been published.

Tensile Strengths.   The tensile strength of abrasive wheel bonds
goes above 2000 pounds per square inch.   Strength and water-resistance
vary. with conditions which have not been fully explained.   A series
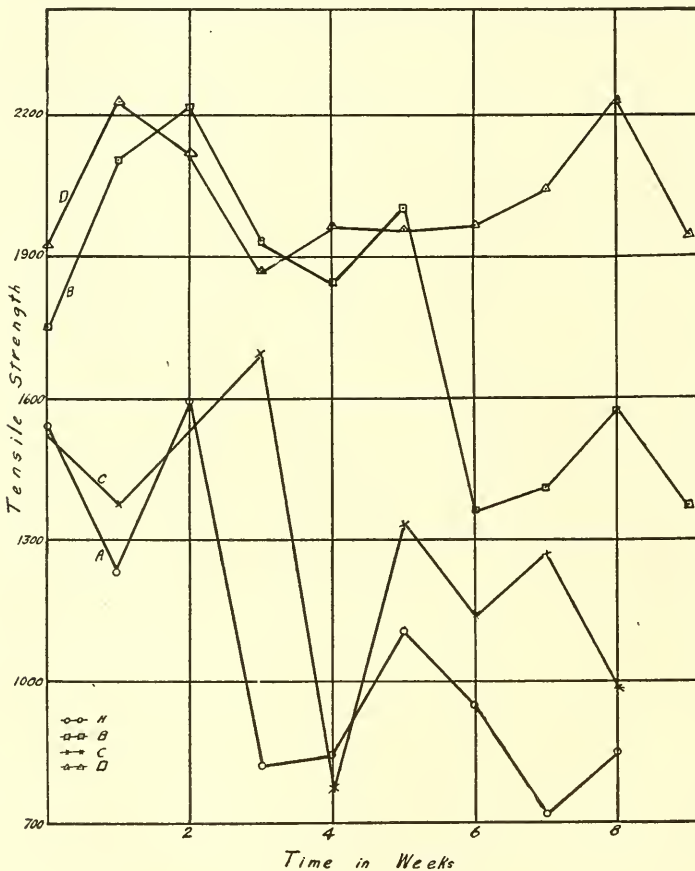
FIG. 82.—Tensile Strengths of Briquets.

of briquets from a mixture made with silicates of identical com-
position but by different processes of preparation gave, on alternate
soaking and draining for 12-hour periods, the tensile strengths shown
in Table 65.   Every effort to distinguish the silicates by chemical
means has thus far failed.   The analyses of four samples, designated A,
B, C, and D, are given below.

TABLE 64. *Composition of Briquets.*

		A	B	C	D
Per cent	Al$_2$O$_3$	0.22	0.29	0.21	0.28
" "	Fe$_2$O$_3$	0.18	0.18	0.17	0.14
" "	CaO	None	None	None	None
" "	MgO	None	None	None	None
" "	Cl	0.07	0.07	0.09	0.09
" "	SO$_3$	0.02	0.02	0.02	Trace
" "	H$_2$O	45.83	45.83	45.31	45.75
" "	SiO$_2$	35.58	35.50	36.29	36.92
" "	Na$_2$O	18.08	18.08	18.20	17.66

TABLE 65. *Tensile Strength of Briquets.*

	A	B	C	D
Dry	1542	1753	1520	1926
1st week	1237	2109	1376	2234
2nd "	1598	2223	....	2121
3rd "	822	1938	1696	1874
4th "	876	1847	767	1967
5th "	1107	2064	1332	1961
6th "	955	1368	1136	1969
7th "	722	1415	1271	2049
8th "	852	1577	981	2237
9th "	....	1378	....	1950

Variation from the Above Formula. Attempts to use silicates of higher and lower relative alkalinity in this process have had little success. Strong wheels which are too soluble can be made with higher alkalinities. Silicate of the type Na$_2$O, 3.3SiO$_2$, though it gives wheels of good strength and grinding properties under conditions of partial dehydration, yields a very weak body when all the water is driven off unless the temperature is raised to a point where sintering begins, when the bond is brittle.

Urtel [11] proposes to make a more water-resistant, though rather brittle wheel, from a mixture similar to the one described above, by firing to 850° to 1100°C.[12]

The limiting factor in making a hard silicate wheel is the amount of silicate which can be introduced.[13, 14] The formula given above is about the maximum to keep a consistency such that the grains slide over each other enough to form a dense body and at the same time prevent the liquid from flowing from one part of the body to another while the wheel is in process. This situation has been met in some

[11] Urtel, Henry, U. S. Pat. 1,243,783 (Oct. 23, 1917).
[12] Tilton, Clarence B., and Milton F. Beecher, U. S. Pat. 1,555,086 (Sept. 29, 1925).
[13] Martin, Harry C., U. S. Pat. 1,310,360 (July 15, 1919).
[14] Power, Henry Robert, U. S. Pat. 1,310,292 (July 15, 1919).

cases by adding powdered dry silicates which dissolve before the water is driven from the wheel.[15, 16]

Solid anhydrous silicate in powdered form, whether the ratio be that of the alkaline silicate, as the $1:2$ ratio is called in the trade, or a ratio of $1:3$ can be slowly hydrated by keeping the moist molded mass warm before drying.[17] Any attempt to make stronger or harder wheels by putting in more silicate as a solution is unsatisfactory because the mass becomes too fluid, the liquid portion tending to leave the upper surfaces and accumulate near the bottom. It is obvious that irregularities in the hardness of the grinding stone constitute a fatal objection.

Silicon Carbide.   All the aluminous abrasives are easily bound by the silicate process, but silicon carbide reacts with some alkaline solutions with the liberation of hydrogen according to the equation: $SiC + 4NaOH + 2H_2O = Na_2SiO_3 + Na_2CO_3 + 4H_2$. Other reactions yielding hydrogen take place between caustic alkali and metallic aluminum or the element silicon which may be present in carbide abrasives. Soluble silicates in solution produce a reaction which, though much less vigorous than the action of caustic alkali, and soon inhibited by the deposition of a silicious film, is sufficient to release appreciable quantities of hydrogen. This gas liberated at the interface between abrasive grain and silicate solution is extremely detrimental to the bond. The evolution of gas can be brought under control by use of an oxidizing agent in the silicate solution. For this purpose permanganates have been found most convenient.[18, 19]

Another method which can be used to reduce the evolution of hydrogen consists of giving the abrasive grains a preliminary treatment with warm dilute sodium hydroxide or sodium silicate and washing. This seems to render the surface less active and allows the silicate to wet the grains sufficiently to form a firm bond.[20] It is advantageous also for aluminous abrasives.[21]

Briquets.

Briquetting of fine iron ore, such as pyrite cinder, and carbonaceous materials, has been undertaken with the aid of silicate binders. Strong,

[15] Johanson, Pehr, and Clarence B. Tilton, U. S. Pat. 1,555,119 (Sept. 29, 1925).
[16] Keever, Paul, U. S. Pat. 1,548,145 (Aug. 4, 1925).
[17] Henkel & Cie., Ger. Pat. 215,328 (March 27, 1924).
[18] Vail, James G., and John D. Carter, U. S. Pat. 1,139,739 (May 18, 1915).
[19] Vail, James G., *Abrasive Ind.*, **2**, 393-394 (1921).
[20] Stowell, Edward R., U. S. Pat. 1,327,448 (Jan. 6, 1920).
[21] Anderson, Harry O., U. S. Pat. 1,400,495 (Dec. 13, 1921).

hard products can be made with 5 to 10 per cent of 40 per cent solutions of the more silicious silicates; but the conditions which give satisfactory water-resistance together with sufficient economy and the desired slagging properties appear not to have been worked out. The silicate bond for coal briquets has the advantages of economy, smokeless burning, and holding the form of the briquet in the fire, and is worth further study.[22, 23]

Modification of Properties.

It is fairly obvious that any of the cements which depend on the drying of the silicate solutions for setting may be modified by substances which alter the behavior of the silicate. Thus glycerin, by retarding the drying, is sometimes useful. Dextrin in like manner imparts its own characteristics to mixtures. Commercial glucose syrup works well in the cold but gels on heating; sugar can be mixed freely with silicate solutions and increases slightly their flexibility. Many highly hydrolized products, such as the adhesive by-product of the manufacture of furfural from corn cobs or that recovered from waste sulfite liquors, may find use for special purposes. The latter must be neutralized with sodium hydroxide to avoid precipitation of the silica. The same is true of most vegetable tanning extracts. Rubber latex which has been stabilized with ammonia mixes smoothly with the silicious silicate solutions and increases resistance to water and flexibility. Shellac can be dissolved in silicate to modify the character of a cement, and other inert materials can readily be thought of which may at times be of use, whether the silicate is to be applied as cement, adhesive or protective film.

Accelerated Setting.

Treating the exposed cement surfaces with strong sulfuric acid soon after the bricks have been placed in position is frequently recommended, in order to cause immediate setting of silicate cements used in acid-proof brick construction. This practice is not consistent with the maximum ultimate strength. The acid causes the gelation of the dissolved silica. If this takes place in the presence of much water the result is a soft gel which contracts on drying and has little bonding power. When drying precedes contact with acid the gel is much stronger and shrinks less, though it never equals the tenacity of the dried silicate solution. Briquets of the first mentioned series, which tested 788 pounds per square inch tensile strength, air-dried, were

[22] Taggart, William P., U. S. Pat. 1,396,603 (Nov. 8, 1921).
[23] Collins, William Frederick, U. S. Pat. 445,568 (July 27, 1908).

soaked for two days in 60° Baumé sulfuric acid, then washed in running water until methyl orange showed no further acidity. They were then taken out and dried in the air at 49°C. The tensile strength was 273 pounds. A mass was thus obtained consisting only of silica in various states of hydration which had been formed at atmospheric temperatures and had a strength equal to a fair 1-2-4 concrete.

ACID-PROOF CEMENTS.

Glover and Gay-Lussac Towers. The technic of building acid-resisting structures with cements of this type involves not only proper
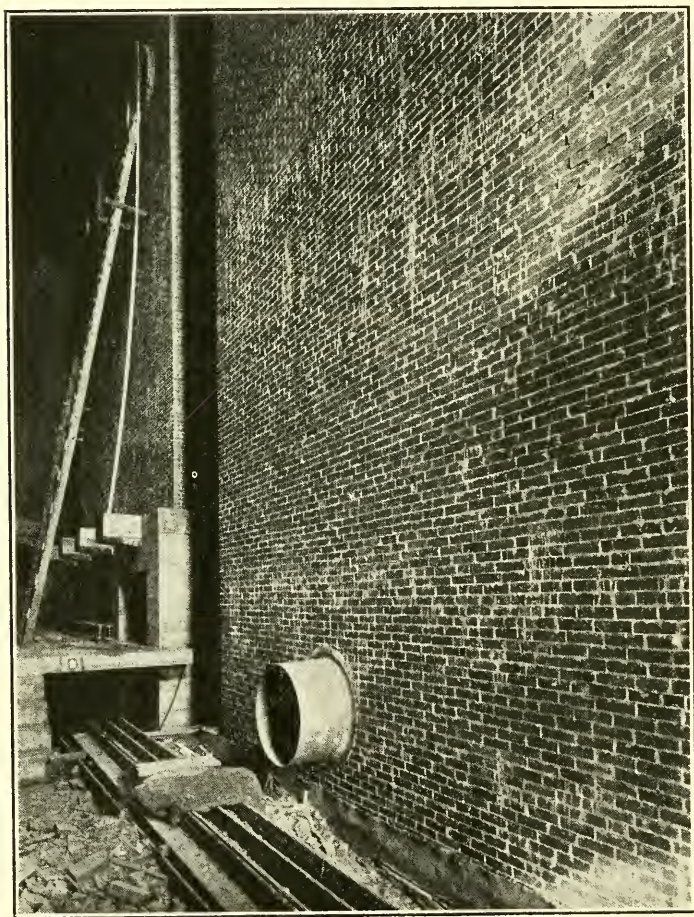
FIG. 83.—The Effect of Building too Rapidly—Cement Squeezed Out by Load Applied before It Was Sufficiently Set.

mixtures but care in laying them. Walls must not be built at such a rate that the cement does not set fast enough to resist the load. The illustration of a Gay-Lussac tower wall from which the unset cement was squeezed shows the result of too rapid building. Joints should not

be thicker than 1/8 inch if possible. Corners should also be braced with wooden forms [24], [25], [26] until the cement has hardened. The illustrations show construction of this sort which has saved large investment for lead in chamber-acid plants. In tower and tunnel concentrators it is good practice to use temperatures above the melting point of lead.

Various clays have been used instead of silica in cements of this character; but so long as they are chemically inert toward the silicate, their usefulness depends upon insolubility in the acid and upon their fitness to yield a mass of maximum density and mechanical strength. Glover and Gay-Lussac towers and even whole chamber systems have been built of brick with the aid of this sort of cement and give very satisfactory service.

Tank linings, absorbing towers, linings for lead chamber bottoms, equipment for mixing and storing acids, acid house floors and molded articles are made with the aid of silicate cements.[27]

Fillers. Other materials which have been recommended for sulfuric acid-resisting cements, such as barium sulfate, asbestos, talc, et cetera, do not seem to give better results than pure silica.[28] Carter[29] found that barium sulfate is somewhat harmful when sulfuric acid is to be retained and may lead to prompt failure with nitric or hydrochloric acid. Of several mixtures used, he found that containing powdered quartz or sand of suitable sizes bound with silicate of ratio 1 : 3.92 and diluted to 34° Baumé to be the most satisfactory.*

TABLE 66. *Resistance of Silicate Cements to Acids.*

Mixtures	Treatment	Results
100 parts powdered silica, 100 mesh	Conc. H_2SO_4	Still hard after 11 months in acid.
	Dil. H_2SO_4	" " " " " " "
50 parts $Na_2O, 3.96SiO_2$	Conc. HCl	" " " " " " "
	Dil. HCl	" " " " " " "
	Conc. HNO_3	" " " " " " "
	Dil. HNO_3	" " " " " " "
Ground Quartz Rock	Conc. H_2SO_4	Hard after 5 months. Softened on edges.
340 parts 20-100 mesh		
220 parts 100 mesh and finer	Dil. H_2SO_4	Still hard after 11 months.
	Conc. HCl	Little soft on edges after 5 months.
146 parts $Na_2O, 3.3SiO_2$	Dil. HCl	Still hard after 11 months.
	Conc. HNO_3	" " " " "
	Dil. HNO_3	" " " " "

[24] Catalog of Maurice A. Knight, Akron, Ohio, p. 17.
[25] *Chem. Ztg.*, **47**, 504 (1923); *C. A.*, **17**, 3083.
[26] Clark, T. S., *Ind. Eng. Chem.*, **15**, 227-230 (1923).
[27] Windsor-Richards, W. E., Brit. Pat. 153,047 (June 24, 1919).
[28] Bassett, Harry P., U. S. Pat. 1,390,327 (Sept. 13, 1921).
[29] From the records of the Philadelphia Quartz Company.
* Cf. page 195.

TABLE 66. *Resistance of Silicate Cements to Acids—(Continued).*

Mixtures	Treatment		Results
750 parts sand	Conc.	H_2SO_4	Much cracked in 2 months.
(Fox River, Ill.)	Dil.	H_2SO_4	Still hard after 11 months.
250 parts kaolin	Conc.	HCl	" " " " "
270 parts $Na_2O, 3.3SiO_2$	Dil.	HCl	" " " " "
	Conc.	HNO_3	" " " " "
	Dil.	HNO_3	" " " " "
500 parts sand	Conc.	H_2SO_4	Softened on edges in 5 months.
50 parts $BaSO_4$	Dil.	H_2SO_4	" " " " " "
137 parts $Na_2O, 3.3SiO_2$	Conc.	HCl	Disintegrated after 1 day.
	Dil.	HCl	Softened on edges in 5 months.
	Conc.	HNO_3	Much softened on edges in 7 days.
	Dil.	HNO_3	Softened on edges in 5 months.
500 parts sand	Conc.	H_2SO_4	Weak and much cracked in 4 days.
100 parts talc	Dil.	H_2SO_4	Still hard after 11 months.
150 parts $Na_2O, 3.3SiO_2$	Conc.	HCl	" " " " "
	Dil.	HCl	A little softened after 11 months.
	Conc.	HNO_3	Still hard after 11 months.
	Dil.	HNO_3	Softened, s o m e w h a t, after 11 months.
500 parts sand	Conc.	H_2SO_4	Very weak in 1 day.
50 parts litharge	Conc.	HCl	Broke up in a few minutes.
185 parts $Na_2O, 3.3SiO_2$			
600 parts sand	Conc.	H_2SO_4	Very weak and cracked in 1 day.
200 parts powdered mica	Dil.	H_2SO_4	Much softened in 5 months.
240 parts $Na_2O, 3.3SiO_2$	Conc.	HCl	Much softened on edges in 5 months.
	Dil.	HCl	Softened in 11 months.
	Conc.	HNO_3	Much softened on edges in 7 days.
	Dil.	HNO_3	Softened in 11 months.
600 parts sand	Conc.	H_2SO_4	Much softened on edges in 1 day.
200 parts fluorspar	Dil.	H_2SO_4	Somewhat softened on edges in 11 months.
242 parts $Na_2O, 3.3SiO_2$	Conc.	HCl	Much softened on edges in 4 days.
	Dil.	HCl	Much softened on edges in 5 months.
	Conc.	HNO_3	Much softened on edges in 7 days.
	Dil.	HNO_3	Much softened on edges in 5 months.
600 parts sand	Conc.	H_2SO_4	Completely disintegrated in 1 day.
60 parts blown petroleum	Dil.	H_2SO_4	Softened on edges in 5 months.
pitch, asphalt base	Conc.	HCl	Completely disintegrated in 1 day.
	Dil.	HCl	Softened in 11 months.
	Conc.	HNO_3	Much weakened in 1 day.
	Dil.	HNO_3	Softened in 5 months.
650 parts anhydrous	Conc.	H_2SO_4	Much disintegrated in 4 days
$Na_2O, 3.3SiO_2$	Dil.	H_2SO_4	Weakened in 5 months.
230 parts $Na_2O, 3.3SiO_2$	Conc.	HCl	Much disintegrated in 1 day.
	Dil.	HCl	Weakened in 5 months.
	Conc.	HNO_3	Much weakened and broken in 4 days.
	Dil.	HNO_3	Weakened in 5 months.

TEMPERATURE RELATIONS.

High Temperature Cements. Cements which are serviceable at higher temperatures than those used for abrasive wheels, but which are required to assume a rigid consistency at atmospheric temperatures, are made from various silicate solutions according to the specific properties desired.[30, 31, 32] Cements which set in the air to form a bond between glass pieces having a tensile strength of about 1,000 pounds per square inch and at the same time capable of withstanding practically without deformation a temperature of 1,100°C., may be made from chromite and soluble silicate either in liquid form or as hydrous readily soluble powder.[33] Clapp[34] adds finely divided ferro silicon.

Various clay refractories mixed with silicate solutions yield gas-tight cements for chemical apparatus, boiler settings, blast furnace stoves, coke oven refractories, flues, regenerator casings for open-hearth furnaces, and other high-temperature work,[35, 36, 37, 38, 39, 40] the efficiency of which is improved by making refractory walls impermeable to gases either by coating the surfaces of the brick to make a glaze under heat or setting them in a cement which will vitrify.[41] Howe[42] determined the effect of various additions to a plastic refractory clay of the following composition:

TABLE 67. *Analysis of Plastic Fire Clay Used.*

Loss on ignition	11.12%
Silica	56.42
Alumina	28.46
Ferric oxide	3.12
Lime	0.52
Magnesia	0.44
Alkalies	0.24
Fusion point, Cone 30.	
	100.32

[30] Willetts, Paul G., U. S. Pat. 1,573,888 (Feb. 23, 1926).
[31] Youngman, Robert H., U. S. Pat. 1,564,394 (Dec. 8, 1925).
[32] Youngman, Robert H., Brit. Pat. 250,480 (Oct. 24, 1925); *C. A.,* **21,** 1172.
[33] Rochow, William, U. S. Pat. 1,576,550 (March 16, 1926); U. S. Pat. 1,606,481 (Nov. 9, 1926).
[34] Clapp, Harry Baker, U. S. Pat. 1,437,584 (Dec. 12, 1922).
[35] For example, Bassett, Harry P., *loc. cit.* and U. S. Pat. 1,390,328 (Sept. 13, 1921).
[36] Meyer, Albert, U. S. Pat. 1,483,468 (Feb. 12, 1924).
[37] Wolcott, E. R., U. S. Pat. 1,617,696 (Feb. 15, 1927).
[38] Reynolds, R. W., U. S. Pat. 1,422,130 (July 11, 1922).
[39] O'Hara, C. M., U. S. Pat. 148,972 (Aug. 9, 1873).
[40] Fulcher, G. S., Can. Pat. 248,315 (March 31, 1925); *Ceram. Abstracts,* **4,** 347.
[41] Holley, Earl, U. S. Pat. 235,505 (June 18, 1925).
[42] Howe, Raymond M., "The Necessity for Care in the Preparation and Use of Fire Clay Mortar," Refractories Manufacturers Association, **1920.**

It is surprising to observe that the effect of sodium silicate is **much** less than other additions tried.   Unfortunately, the exact composition of the silicate is not available.
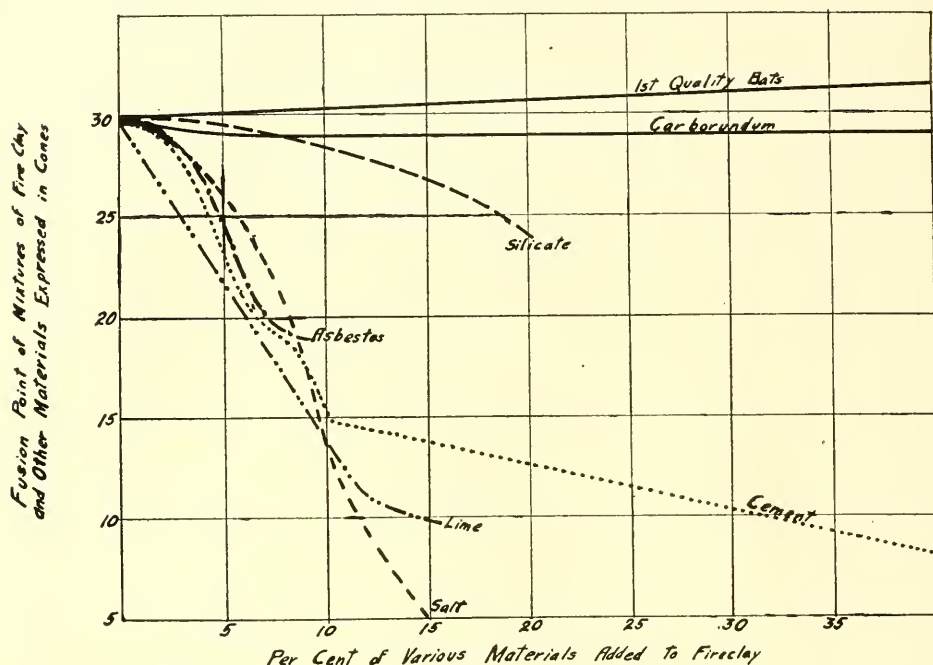
Fig. 84.—Effect on the Melting Temperatures of Additions to Fire Clay.

The temperature which any clay will resist is doubtless reduced by mixing it with a silicate solution, but if this is done with regard to the conditions to be met, many useful cements can be made and built into refractory walls which stand temperatures much above the melting temperature of the cement by itself.   As the silicate penetrates the refractory it becomes associated with larger and larger quantities of clay so that in practice higher temperatures are resisted than would be found by examination of the cements alone.   It is probably unwise to use silicate cements where refractory bricks are to be used close to their melting temperatures, but a great many linings are used where the temperature is safely below the limit of the brick and here the advantages of the silicate cements are great.[43, 44, 45]   Cements for setting refractories in iron stoves are chosen rather for their plasticity and freedom from shrinkage than in consideration of their melting temperatures because even those cements which are made with the slow

[43] Société Générale des Nitrures, Brit. Pat. 1961 (June 20, 1912).
[44] Jones, D., and W. Emery, *Gas J.*, **163**, 157-159 (1923) ; *Gas World*, **78**, 646.
[45] Wakem, F. J., *Ind. Eng. Chem.*, **15**, 893-894 (1923).

setting alkaline silicates are sufficiently refractory to stand the conditions of a house heating furnace.

Meloche [46] has elaborated a technic for protecting and repairing refractory surfaces by coating them with silicate-clay mixtures and causing thin layers to vitrify with the aid of a blow torch.[47]

Silicate solutions and clay are used to repair the saggers or earthen cases in which pottery is burned. The picture shows pieces of such ware which have been broken at other places than the mended joint.
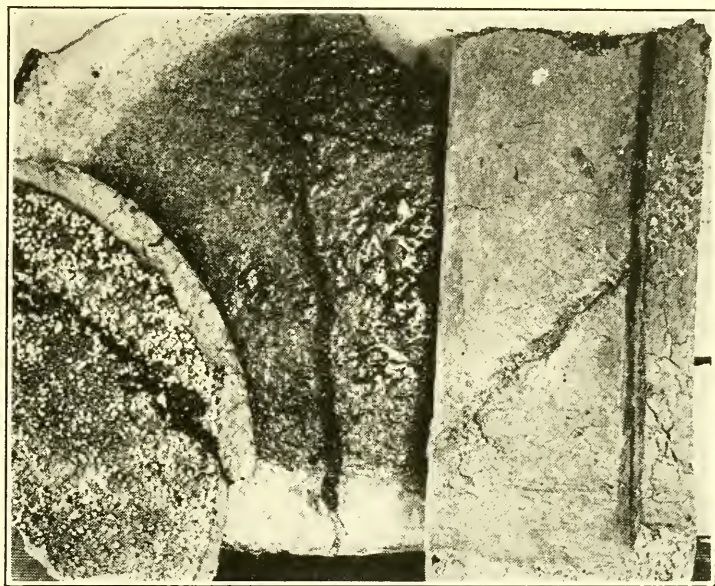
Fig. 85.—Saggers Repaired with Silicate Cement.

It may be recognized that the three pieces represent top, side, and bottom of the sagger. Where the breaks are simple it is cheaper to repair them with cement than to grind the broken sagger and make the body into new ware which must be burned before use. A satisfactory formula for this purpose is

$Na_2O, 2.5SiO_2$ at 45° Baumé mixed to the consistency of thick cream with kaolin.

Drying. The temperature at which a silicate cement is to be used will affect the choice of the type of silicate. The set which results from loss of moisture will reach a maximum and decline before all the water has been expelled by rising temperature. Cements made from viscous silicates are subject to intumescence or swelling when heated suddenly, and even with gradual heating this is likely to occur

[46] U. S. Pat. 1,534,237 (April 21, 1925).
[47] Moldenke, Richard, *Chem. & Met. Eng.,* **29**, 231-232 (1923).

at about 500°C. if the body is not sufficiently porous to allow the water to escape quietly. After the water has been completely driven off, strong bonds may be formed by the sintering of the soluble silicate with or without reaction between it and the filler. The different effects of ascending temperature on three silicates are indicated by the chart. All tests were made after the briquets had cooled. The most alkaline
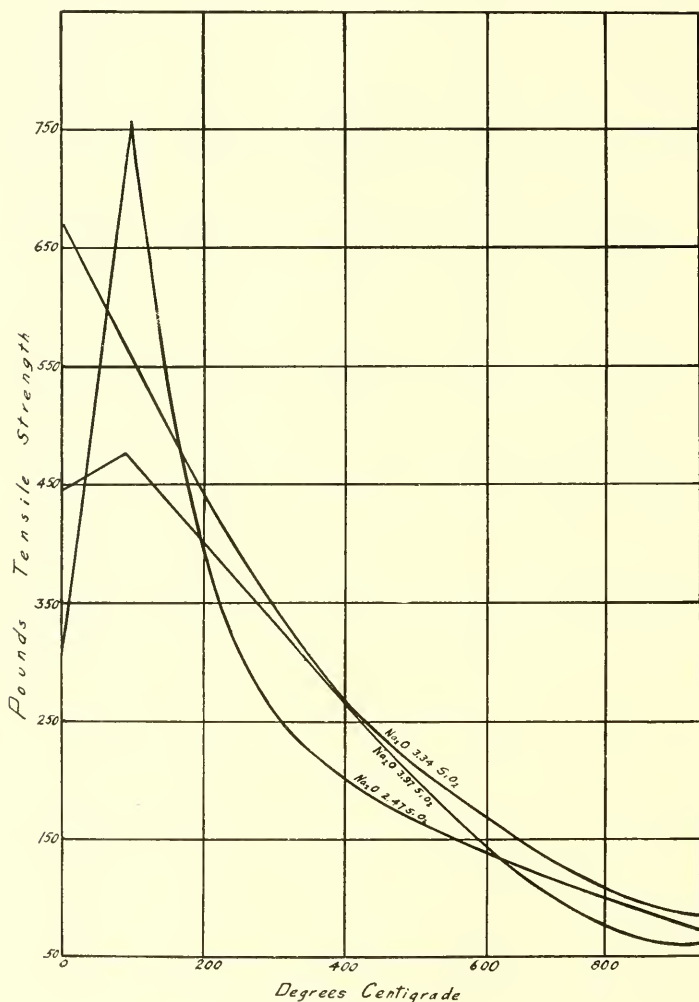
FIG. 86.—Effect of Rising Temperature on Strength of Briquets Containing 100 Parts Calcined Fire Clay and 33.3 Parts Silicate Solution.

of the three ratios examined is used particularly for refractory linings, where the practice is to apply a preliminary drying treatment below 500°C. and to effect the heating above the sintering temperature rapidly to form a ceramic bond. This behavior was recognized by Tone,[48]

[48] U. S. Pat. 1,042,844 (October 29, 1912).

who reported that the maximum strength of the silicate developed between 204° and 315°C. He thus produced a lining which was bonded by sintered clay at the hottest parts of the furnace and was yet satisfactorily strong at the cooler points. Smaller amounts of silicate than those used in the preceding experiments may account for a small shift in the temperature giving maximum strength.

Kaolin Cements.

Spark Plugs. Staley [49] investigated a series of soluble silicate mixtures with silica, aluminum oxide, barium sulfate, and kaolin, raw and calcined, for cements to be used in making a gas-tight joint between a metallic electrode and a porcelain spark plug body. Only one type of silicate solution, $Na_2O, 3.3SiO_2$, was used; but the temperatures se-

TABLE 68. *Effect of Cements on Electrode Wires.*

Cement No.	Sodium Silicate 40° Baumé Cubic Centimeters	Water Cubic Centimeters	Solid Grams	Kind	Effect of Oxidation	Heating to 1000°C. Description
1	5	5	30	Powdered silica	Very bad	Hard, strong, slightly porous; part of material had run down the wire.
2	10	..	30	Powdered silica	Very bad	Hard, strong, slightly porous; part of material had run down the wire.
3	5	2	30	Barium sulfate	Eaten through	Part of material had melted and run down wire, leaving a hard blue mass behind.
4	7	..	30	Barium sulfate	Eaten through	Part of material had melted and run down wire, leaving a hard blue mass behind.
5	5	5	30	Kaolin	None	Hard, strong, slightly porous.
6	10	..	30	Kaolin	None	Hard, strong, not porous.
7	5	9	{ 15 { 15	Kaolin Aluminum oxide	Very bad	Soft, weak, porous
8	10	4	{ 15 { 15	Kaolin Aluminum oxide		Soft, weak, porous, very bad.

[49] *Bur. Standards Tech. Paper,* **155** (1920).

lected, 500° and 1000°C., give rise to reactions which do not take place at atmospheric temperatures. Pellets of the various cement mixtures were dried on a nickel alloy electrode wire and heated in an oxidizing atmosphere. The superiority of the raw kaolin mixture as shown by the table was evidently due to its ability to wet the surface of the wire and then to coat it with a substance which was dense and sufficiently viscous at all stages of the heating process to remain in place.

In contrast to the dense viscous coating made with raw kaolin, the particles of which are very small, barium sulfate yielded a heterogeneous body which liberated sodium sulfate. This coating is thinly fluid at 1000°C. and oxidation proceeded rapidly.[50]

Silicate and silica afforded poor protection because the mixtures were too fluid at the maximum temperature.

Staley attributed the porosity of cements containing aluminum oxide or calcined kaolin to reaction with the silicate in the cold. It would have been interesting had the work been extended to other types of silicate solutions and to different physical conditions of the filling materials.

Silicate Cements in Case Hardening. Silicate cements applied to steel surfaces to keep certain portions soft during case hardening were studied by Wood and McMullan.[51] Presumably a silicate similar to that used by Staley was employed. These workers found it possible to secure better protection with asbestos and sodium silicate or with aluminum oxide and sodium silicate than with any mixture involving kaolin. The exposures were, of course, different, but it would appear that in each case an impermeable viscous layer is needed, and one wonders why the kaolin mixture permitted the passage of carbon but resisted oxygen, while with aluminum oxide the relation was reversed. Many silicate glasses disperse carbon and become highly colored, as the glass maker often finds to his sorrow, and the special action of the kaolin coating toward carbon may account for its unfitness as a protection against case hardening. In this connection it may be worth while to note the fact that highly aluminous bricks in a glass furnace usually burn to a dark chocolate color, while more silicious types remain light colored when exposed to the same atmosphere.

Wood concluded that finely ground asbestos and silicate solution (believed to be 40°Baumé $Na_2O, 3.3SiO_2$) gave perfect protection at 950° and 995°C. in layers 1 mm. thick when the percentage of silicate was

[50] Seger, Herman A., "Collected Writings," **2**, Easton, Pa.; Chemical Publishing Co., 636.
[51] *Chem. & Met. Eng.*, **26**, No. 23, 1077 (1922).

67 or more, and that mixtures with aluminum oxide were also good but had to be used in somewhat thicker layers. The removal of these adherent hard coatings proved to be a problem. Quenching, a number of times if necessary, was satisfactory in most cases. The coatings were also broken down and loosened by dipping in molten caustic soda or by heating in molten calcium chloride, followed in each case by immersion in water. The coatings were not found to prevent decarburizing or absorption of carbon. It may well be that the kaolin mixture would be the more useful, as from Staley's work it appears to afford better protection against oxygen. There is an excellent bibliography attached to Wood's article. Other mixtures have been tried by various investigators.[52, 53, 54]

Copper plating is a satisfactory method of locally preventing case hardening by carburization and it has been proposed to use finely divided copper in a silicate cement.[55, 56] The results are not known to be better than a suitable silicate mixture with the less costly clays.

CASTING METALS.

The art of casting metals has frequent use for the binding properties of soluble silicates to form molds or to increase the resistance of those parts of sand molds most likely to be eroded or deformed by the flowing of hot metal.[57] The amount of silicate to mix with molding sand must be chosen with regard to the porosity desired, to permit the escape of gases, and to its property of not burning out when heated, as organic binders do. Sand molds have also been coated with metals, such as chromium, comminuted and mixed with silicate which holds them in place until they can alloy with the metal cast into the mold, giving it a specially resistant surface.[58] Permanent metal molds for automatic casting machines have been made by lining cast iron molds with mixtures of silicates and refractory clays. Meloche prevents the metal from sticking to the silicate cement by applying a smoky flame after each casting operation.[59, 60]

[52] Dickens, E. J., Brit. Pat. 185,564 (Sept. 14, 1922).
[53] Bickley, A., U. S. Pat. 1,432,523 (Oct. 17, 1922).
[54] Whyte, Samuel, U. S. Pat. 1,366,305 (Jan. 18, 1921).
[55] Gailbourg and Ballay, *Rev. Métal.,* 19, 222-226 (1922).
[56] For example: Whinfrey, Charles G., U. S. Pat. 1,567,632 (Dec. 29, 1925).
[57] Wilhelmy, Odin, U. S. Pat. 1,544,710 (July 7, 1925).
[58] Mitchell, Walter M., U. S. Pat. 1,545,438 (Sept. 24, 1924).
[59] Meloche, D. H., U. S. Pat. 1,453,593 (May 1, 1923) ; U. S. Pat. 1,506,130 (Aug. 26, 1924).
[60] Udale, Stanley M., U. S. Pat. 1,505,176 (Aug. 19, 1924).

MOLDED ARTICLES.

Silicate has been mixed with many kinds of fibrous materials to form plastic masses.[61, 62, 63, 64, 65] The process of Lowe for making molded articles for heels of shoes and like materials by mixing filaments of oak wood with a silicate solution, pressing into molds and drying, may be taken as typical.[66] Fibrous materials with silicate for making molded articles require a neat adjustment between concentration and alkalinity of the silicate on one hand, and pressure on the other, if dense articles which can be quickly formed and will not crack on drying are to result. Cotton stalks, sawdust, residual fiber from the process of making furfural from corn cobs and many others have been investigated.[67, 68] In molding ceramic materials, silicate is frequently employed as the binder.[69]

MISCELLANEOUS CEMENTS.

For Insulation. Cements of essentially similar composition have been used for various insulating purposes,[70, 71, 72, 73, 74, 75] such as covering the coils of resistance heaters to keep them spaced. Silicate and powdered fused aluminum oxide give good results as long as they remain dry. Soapstone and powdered silica have also yielded cements useful at low temperatures,[76] though where oxidation is a factor the kaolin cement is preferable. If these cements are exposed for extended periods to a humid atmosphere, their electrical resistance is reduced but can be readily restored by drying. The effect of moisture is somewhat reduced by mixing the silicate with an ammoniacal solution of shellac or gum solutions.[77, 78, 79]

[61] Haas, Nelson R., U. S. Pat. 1,618,875 (Feb. 22, 1927).
[62] Ritchie, J. A., Brit. Pat. 229,092 (Feb. 15, 1924) ; *Ceram. Abstracts*, **8**, 331 (1925).
[63] Wheeler, James A., U. S. Pat. 539,928 (May 28, 1895) ; U. S. Pat. 625,372 (May 23, 1899).
[64] Naylor, Isaac, U. S. Pat. 1,573,734 (Feb. 16, 1926).
[65] Bartlett, Francis A., U. S. Pat. 1,484,370 (Feb. 19, 1924).
[66] Lowe, U. S. Pat. 1,532,908 (April 7, 1925).
[67] Stryker, G. B., and Frank A. Mantel, U. S. Pat. 1,436,061 (Nov. 21, 1922).
[68] Stowell, E. R., U. S. Pat. 1,524,676 (Feb. 3, 1925).
[69] Berry, E. R., U. S. Pat. 1,131,463 (March 9, 1915).
[70] Gerloch, Oscar, U. S. Pat. 1,468,149 (Sept. 18, 1923).
[71] Slepian, Joseph, U. S. Pat. 1,638,888 (Aug. 16, 1927).
[72] Cook, Frank J., U. S. Pat. 1,393,346 (Oct. 11, 1921).
[73] Stowell, E. R., U. S. Pat. 1,382,329 (July 14, 1921).
[74] Covell, Bradford S., U. S. Pat. 1,610,203 (Dec. 7, 1926).
[75] Meloche, Daniel H., U. S. Pat. 1,505,215 (Aug. 19, 1924) ; Brit. Pat. 235,503.
[76] Menuez, Anthony E., U. S. Pat. 438,698 (Feb. 24, 1890).
[77] Barringer, L. E., U. S. Pat. 1,423,985 (July 25, 1922).
[78] Grote, L., U. S. Pat. 789,607 (May 9, 1905).
[79] Norman, J. T., U. S. Pat. 949,493 (Feb. 15, 1910).

Carbon Arcs. One of the few cases in which a potassium silicate performs a service not to be equaled by a suitable adaptation of sodium silicate is as a binder for the carbon pencils used as electrodes in arc lamps. Not only is the color of the potassium flame preferred, but a longer arc and more efficient illumination are secured in this way. The carbon, in a finely divided state, is mixed with a silicate solution of the approximate composition $K_2O, 3.25SiO_2$, extruded in a pasty condition, and baked for drying.

Other wares such as slate pencils may be made from appropriate mineral powders by mixing them to the consistency of dough and extruding them through apertures of the desired form. A firm texture is usually secured with less than 10 per cent anhydrous weight of $Na_2O, 3.3SiO_2$. If slow setting is desired in this type of mixture, $Na_2O, 2SiO_2$ may be chosen.

Asbestos Cements—Alignum. Wheeler[80] prepared a structural material by preparing a stiff dough from short asbestos fiber with or without other mineral matter. This was pressed into form and baked at 200° to 270°C. to form a hard substance, called Alignum, which could be used for doors and trim but which could at the same time be worked with wood-cutting tools. $Na_2O, 3.3SiO_2$ was used and satisfactory fire doors were made, though at somewhat greater cost than steel doors, which were commercially perfected at a later time.

Since this behavior of Alignum[81] is analogous to that of other silicate cements, data obtained from tests on this material are of value.[82, 83]

Strength tests were made by supporting slabs on knife edges and applying a load at the center. The slabs were afterwards hammered with a sledge hammer and found to be tough.

In order to test the fire-resisting quality of Alignum doors, they were subjected to the action of a fire of cord wood, maintained at a temperature of about 930°C. for one hour. During this time the door showed no tendency to warp, and prevented perfectly the escape of fire or smoke through or around it. Radiation of heat was at all times small, the back of the door remaining comparatively cool. The fire was extinguished by a stream of water aimed directly at the red-hot door. At the end of the test, the Alignum remained intact. It had not warped more than $\frac{1}{2}$ inch, and that only in one corner. The door was practically as good as new.

[80] U. S. Pat. 539,928 (May 28, 1895).
[81] Catalogue of the Alignum Asbestos Lumber Company, New York, **1908**, p. 20.
[82] Imschenetzky, A., U. S. Pat. 631,719 (Aug. 22, 1899).
[83] Michell, H. C., U. S. Pat. 774,947 (Nov. 15, 1904).

TABLE 69. *Strength Tests of Alignum.*

Test No. 1.
1″ × 8″ slab.
Supports 48″ apart.

Load, Lbs.	Deflection, Inches
100	.0
200	.125
300	.500
0	.0
350	.75 failed by cracking

Test No. 2.
2″ × 10″ slab.
Supports 46″ apart.

100	.0
200	.0
400	.032
500	.032
600	.063
700	.063
800	.094
900	.125
1000	.125
0	.0 no set
1100	.157
1200	.157
1300	.188
1400	.188
1500	.313
0	.0 no set
1700	.313
1900	.313
2000	.313
0	.0 no set
2500	.438
0	.031 permanent set
3000	.688
3020	Broke

Tests on dielectric strength and the resistance of Alignum showed that although a fairly good insulator when dry, it absorbed moisture readily, thus lowering the dielectric strength and resistance and rendering the material unreliable. Dielectric strength was measured by a gradually increasing A.C. potential applied between electrodes ¾ inch in diameter, with rounded edges, with the following result: on ¼ inch samples, five tests showed the break-down voltages to be 900, 1200, 1300, and 1500 volts, and on a ⅝ inch sample, two tests gave values of 1600 and 1650.

Specific resistance figures (resistance in ohms of a one centimeter cube of the material) are given in table on opposite page.

TABLE 70. *Electrical Resistance of Alignum.*

Time	Temp.	Sample $\frac{1}{4}''$ Thick Specific Resistance	Sample $\frac{5}{8}''$ Thick Specific Resistance
Oct. 12, 7:30 A.M.	20°C.	7.73×10^7	3.21×10^6
	30	3.16×10^7	1.20×10^6
	60	9.20×10^7	. . . .
	91	3.07×10^8	. . . .
	112	1.00×10^9	1.74×10^6
11:55	140	1.01×10^{10}	4.23×10^7
2:13 P.M.	107	4.77×10^{10}	1.50×10^9
3:37	45	1.38×10^{12}	9.70×10^{11}
5:00	30	1.07×10^{12}	8.21×10^{10}
Oct. 13, 10:00 A.M.	18	1.48×10^{11}	2.30×10^{10}
Oct. 23, 2:00 P.M.	25	6.68×10^9	7.91×10^8

The fibrous character of asbestos [84, 85, 86] has caused its frequent insertion in silicate cement formulas, but because the silicate hardens around the individual fibers their yielding character is greatly reduced and the mixture is more brittle than might be expected. Exception to this is found in cases where the spaces between the fibers are not completely filled with silicate solution, but such a cement is apt to be weak.[87] An interesting use of an asbestos-silicate composition is given by Benner.[88]

Asbestos is not wholly inert toward silicate solutions. It is notably impossible to determine by analysis alone what ratio of silica to soda existed in a silicate from which a cement containing asbestos was made. This is also the case when any hydrous, easily soluble, form of silica is present.

CEMENTS WHICH SET BY CHEMICAL REACTION.

LIME MORTARS.

Gilmore [89] experimented with mortars containing lime, sand, and soluble silicate, and in spite of vigorous recommendation by Kuhlmann, came to the conclusion that the result is an inevitable loss of strength. It has, however, been used for cements in which maximum strength was not required.[90]

[84] Michell, Henry Colbeck, U. S. Pat. 714,947 (Nov. 15, 1904).
[85] Bartlett, Francis A., U. S. Pat. 1,598,636 (Sept. 7, 1926).
[86] Imschenetzky, Alexander, U. S. Pat. 631,719 (Aug. 22, 1899).
[87] Vorländer and Schilling, *Ann.*, **310**, 369 (1900).
[88] Benner, R. C., U. S. Pat. 1,495,568 (May 27, 1924).
[89] Gilmore, Q. A., "Limes and Hydraulic Cements," 4th ed., New York: D. Van Nostrand Co., 1874, p. 287.
[90] Plenty, J., Brit. Pat. 3,458 (March 11, 1886).

TABLE 71. *Effect of Silicate on Adhesive Strength of Lime Mortar.*

The adhesion to bricks cemented together transversely.

For mortar of Lime paste 1.0 / Sand 3.0   . . . .   93⅗ lbs.

For mortar of Lime paste 1.0 / Sand 3.0 / Soluble glass .125   . . . .   57¼ lbs.

TABLE 72. *Effect of Silicate on Tensile Strength of Lime Mortar.*

Mortar	Composition of Mortar, in Volumes					Weight in lbs. Supported before Breaking
1.	Lime paste, 1.0	sand, 2.0	soluble glass, .11			40
2.	" " 1.0	" 2.0	" " .11			54
3.	" " 1.0	" 2.0				77⅔
4.	" " 1.0	" 2.0				67⅔
5.	" " 1.0	" 3.0				65
6.	" " 1.0	" 3.0	" " .08			24½
7.	" " 1.0	" 3.0	" " .10			23
8.	" " 1.0	" 3.0	" " .125			18
9.	" " 1.0	" 3.0	cement paste, .50			182⅔
10.	" " 1.0	" 3.0	" " .33			166⅔
11.	" " 1.0	" 3.0	" " .25			92
12.	" " 1.0	" 3.0	" " .166			94⅔

CHARACTERISTICS.

When silicate solutions are dried in the presence of inert substances, the cement may be regarded as a mass of particles adhesively united; and its character must relate quite definitely to the original components. In the case of calcium hydroxide another factor enters. The silicate tends to precipitate or gel, a rapid rise in viscosity takes place, and a quick-setting paste is formed. A great variety of substances react with silicate solutions and when the process takes place in a plastic mass the same general effect follows; but it may take place slowly or fast, according to the materials and conditions chosen.[91] It is rarely advisable to use enough of the reacting ingredient to decompose the silicate completely, so that the great majority of silicate cements are alkaline.

Setting caused by chemical reaction is usually accompanied by loss of ultimate strength and by increase of resistance to water, for silica gels are insoluble. Their strength is greatest when they are formed in the presence of little water. They are solids, while the soluble silicate is liquid even when so viscous as to appear perfectly rigid. A quality of toughness inheres in cements in which soluble silicate remains as such so long as any water is present. Rock-like masses of hydrated silicate show a resilience suggestive of rubber. The rebound of a sledge or cutting tool driven into them will amaze the uninitiated.

[91] Behrens, George E. and Josef Veit, U. S. Pat. 1,063,939 (June 3, 1913).

Addition of Acids and Salts Which React Quickly.

It has been proposed to improve the character of cements made from silica or clay, such as those used to resist acid, by adding small amounts of acids or acid salts. Wedge [92] uses sodium bisulfate or nitre cake, and Meigs [93] uses chlorides, nitrates, phosphates or sulfates of weak bases. Holley and Webb [94] use calcium sulfate or lead carbonate for the same purpose.[95] The result is in each case the same,—partial gelation, increased speed of set, increased resistance to water, and lower ultimate strength. Unless time is of extraordinary importance these mixtures are inadvisable.

Calcium Carbonate.

This criticism does not apply with the same force to substances which react slowly. Kuhlmann [96] recommended mixtures of silicate solutions with powdered marble for the repair of statuary. Von Fuchs [97] suggested mixtures of silicate solutions and calcium carbonate for cements. Limestone, chalk, marble dust, and precipitated forms of calcium carbonate have been used for making plastic bodies for diverse uses ranging from roadways [98, 99] to fine imitation marble [100] for decorative use. It remained for Carter,[101] however, to make the observation that reaction between silicate solution and calcium carbonate is a function of the ratio of sodium oxide to silica in the silicate. $Na_2O, 3.3SiO_2$ may be mixed to a viscous state with powdered chalk and in a closed container the viscosity, a sensitive index of reaction in a silicate solution, remains unchanged for days or even weeks. When $Na_2O, 2SiO_2$ is substituted, a rise in viscosity may be noted in a few hours and proceeds steadily until the mass becomes solid. This difference explains numerous apparent contradictions in the literature. Thus Paterson's patent [102] in which a road material consisting of calcium carbonate and alkaline silicate is described may proceed according to his description and form an in-

[92] U. S. Pat. 1,220,575 (March 27, 1917).
[93] Meigs, Curtis C., U. S. Pat. 1,237,078 (Aug. 14, 1917) ; U. S. Pat. 1,252,013 (Jan. 1, 1918).
[94] Holley, A. E. and H. W. Webb, U. S. Pat. 1,287,995 (Dec. 17, 1918) ; U. S. Pat. 1,288,413 (Dec. 17, 1918).
[95] Chance and Hunt, Brit. Pat. 112,966 (July, 1919) ; *Chim. Ind.*, **2**, 816.
[96] *Compt. rend.*, **41**, 980-3, 1029-35 (1855).
[97] *Dingler's polytech. J.*, **142**, 365-392 (1927) ; Abst. *Chem. Zentr.*, **28**, 86-90.
[98] "Silicate-Macadam Roads," Northwich, England: Brunner, Mond & Co., Booklet 271, **1927**, p. 6.
[99] Lawton, C. F., U. S. Pat. 594,113 (Nov. 23, 1897).
[100] Kallauner, O., *Chem. Ztg.*, **33**, 1174-1175 (1909).
[101] Carter, John D., patent applied for.
[102] U. S. Pat. 1,042,474 (Oct. 29, 1912).

soluble mass slowly under the influence of carbon dioxide of the air if a silicate of low relative alkalinity $(1:3.3)$ is employed, or more rapidly and certainly if the ratio between Na_2O and SiO_2 is $1:2$. As a practical matter, the former type silicate which Paterson used was frequently washed away by rains before any appreciable reaction had taken place. The effort to increase the rate or extent of reaction between soluble silicates and calcium carbonates [103, 104] by adding various forms of sugar, which would be expected to help bring the lime into solution, have been found not nearly so effective as proper regulation of the composition of silicate itself.

Wall Board. Where conditions permit the application of heat, reaction between silicate solution and calcium carbonate may be secured in a short time. A wall board consisting of a mixture of finely ground calcium carbonate and a silicate solution laid as a plastic mass between two layers of paper, and heated at a temperature below that which would carbonize the paper, exhibits a very desirable combination of strength and light weight, for the cement expands by the liberation of steam into an intumescent mass. It compares favorably with gypsum cements, which have been widely used in wall boards.

Roadways. Roadways consisting of coarse stone set in a matrix of silicate mortar have been built in many countries.[105, 106, 107, 108] Under the most favorable conditions they are a great improvement on water-bound macadam construction but are not adapted to carry the highest concentrations of heavy and fast moving traffic encountered on modern trunk highways.

A typical silicate road may be made from limestone dust mixed with Na_2O, $3.3SiO_2$ 1.38 specific gravity ($40°$ Baumé) at the rate of about 26 gallons per cubic yard. Enough water is used to make a rather stiff grout. This is either laid on the compacted road base, covered with two-inch stone and rolled, or mixed with the larger stone before rolling.

In this way 100 pounds of silicate will bind about 10 square yards of road 4 inches thick. Soft limestone is to be preferred because it compacts better and it has been found that some of the alkali of the silicate penetrates the stone leaving a more silicious layer at the surface, which thereby becomes less affected by water. For secondary service

[103] Butterfield, John Cope, U. S. Pat. 808,339 (Dec. 26, 1905).
[104] Paterson, Edward Alfred, U. S. Pat. 987,597 (March 21, 1911) ; U. S. Pat. 996,513 (June 27, 1911).
[105] Peter, A., *Schweiz. Z. für Strassenwesen*, **12**, No. 3, 32 (1926).
[106] Anon., *Schweiz. Z. für Strassenwesen*, **11**, No. 24, 303 (1925).
[107] Caldana and Santambrogio, "Contributo Alla Soluzione del Problema della Strada," Milano, **1926.**
[108] Gaelle, M., "Revelement des Chaussees" (3rd Note, Paris, 1924).

these roads have a place, especially in localities where the most suitable limestones are available. Except in arid climates, however, it is usually impossible to retain a strength of matrix equal to Portland cement though this is easily done with a silicate cement which can be kept dry.[109]

Special Cements.

Great numbers of silicate cements containing fibrous ingredients have been proposed for fireproof plastics, insulating compounds, structural materials, and the like.[110-125] Others that do not contain fibrous materials are used for similar purposes and for the protection of surfaces.[126-139]

Bituminous Materials.

Various attempts have been made to combine the advantages of bituminous substances with those of silicate cements by emulsifying them.[140, 141, 142] It is possible in this way to produce strong, uniform

[109] Wernekke, *Asphalt Teerind Ztg.*, **26**, 470-471 (1926) ; *C. A.*, **21**, 1173.
[110] Keener, Francis M., U. S. Pat. 1,133,380 (Mar. 30, 1915).
[111] Mitchell, Ardon, U. S. Pat. 1,408,760 (Mar. 7, 1922).
[112] Pater, Carl J., U. S. Pat. 1,067,542 (July 15, 1913).
[113] Herbert, Arthur W., U. S. Pat. 1,303,313 (May 13, 1919).
[114] Dunstan, William, U. S. Pat. 1,445,204 (Feb. 13, 1923).
[115] Beadle, George W., U. S. Pat. 1,125,445 (Jan. 19, 1915).
[116] Armstrong, Morgan K., U. S. Pat. 1,076,261 (Oct. 21, 1913).
[117] Oelhafen, John Walter, U. S. Pat. 1,564,706 (Dec. 8, 1925).
[118] Stryker, George B., and Frank A. Mantel, U. S. Pat. 1,436,061 (Nov. 21, 1922).
[119] Lefebure, Victor, U. S. Pat. 1,650,080 (Nov. 22, 1927).
[120] Lefebure, Victor, Brit. Pat. 268,851 (April 17, 1927).
[121] Lennig, Albert M., U. S. Pat. 653,101 (July 3, 1900).
[122] Weintraub-Schnorr, Naum, U. S. Pat. 606,751 (July 5, 1898).
[123] Olney, George, U. S. Pat. 627,008 (June 13, 1899).
[124] Benner, Raymond C., U. S. Pat. 1,573,369 (Feb. 16, 1926).
[125] Hoss, Charles, U. S. Pat. 1,111,021 (Sept. 22, 1914).
[126] Stowell, E. R., U. S. Pat. 819,467 (May 1, 1906).
[127] Willett, Walter E., U. S. Pat. 1,454,780 (May 8, 1923).
[128] Ebbesen, Poulsen Mads, U. S. Pat. 1,570,953 (Jan. 26, 1926).
[129] Suss, Herman M., U. S. Pat. 1,041,526 (Oct. 15, 1912).
[130] Miller, W. E., U. S. Pat. 430,766 (June 24, 1890).
[131] Gauthier, L., Brit. Pat. 128,905 (May 15, 1919).
[132] Schlotterer, G. K., and R. H. Youngman, U. S. Pat. 1,643,181 (Sept. 20, 1927).
[133] Morse, Waldo G., U. S. Pat. 1,392,074 (Sept. 27, 1921).
[134] Dougal, J. W., U. S. Pat. 1,639,629 (July 19, 1927).
[135] Boxer, Frederick N., U. S. Pat. 430,766 (June 24, 1890).
[136] Amies, Joseph H., U. S. Pat. 1,470,674 (Oct. 16, 1923).
[137] Pennington, H. R., U. S. Pat. 1,583,169 (May 4, 1926).
[138] Britton, R. P. L., U. S. Pat. 1,477,938 (Dec. 18, 1923).
[139] Kelly, George, U. S. Pat. 830,329 (Sept. 4, 1906) ; U. S. Pat. 870,367 (Nov. 5, 1907).
[140] Paterson, E. A., U. S. Pat. 1,171,236 (Feb. 8, 1916).
[141] Vail, James G., U. S. Pat. 1,206,056 (Nov. 28, 1916).
[142] Kelly, G., U. S. Pat. 882,891 (March 24, 1908) ; U. S. Pat. 882,890 (March 24, 1908).

bodies; but the resistance to water is disappointing. The property of silicate solutions which enables them to wet oily surfaces has found use in other processes though it is a serious disadvantage here.

MIXTURES CONTAINING PORTLAND CEMENT.

Setting Time.[143, 144]   The relation between silicate solutions and Portland cement has received attention from numerous experimenters.[145, 146, 147]   Ordinary Portland cement reacts at once with solutions containing more than three mols of silica and more slowly with those containing two or less.   The effect of adding small amounts to the gauging water is therefore to increase the speed of set and to reduce the ultimate strength, as indicated in Table 73:

TABLE 73. *Setting Time and Tensile Strengths.*[148]
Na$_2$O, 3.3SiO$_2$, 42.89° Baumé

		Tensile Strength	
	Setting Time	After 7 Days	After 28 Days
		lbs. sq. in.	
A	Briquets gauged with plain water.		
	Initial setting time = 15 minutes		
	Final setting time =145 "	Av. 616	783
B	Briquets gauged with 2% sodium silicate.		
	Initial setting time = 5 minutes		
	Final setting time = 35 "	638	720
C	Briquets gauged with 6% sodium silicate.		
	Initial setting time = 5 minutes		
	Final setting time = 30 "	551	605
D	Briquets gauged with 10% sodium silicate.		
	Initial setting time = less than 5 minutes		
	Final setting time = 25 minutes	406	468

TABLE 74. *Setting Time.*

Silicate			
0		Over 6 hours	
1½ g.	148½ cc. H$_2$O	" 6 "	
4½ "	145½ " "	Began in 5 "	(approximately)
7½ "	142½ " "	" " 4 "	"
15½ "	136 " "	" " 3 "	"

Pretty firmly set in 4½ hours.
Using 30 g. to 120 cc. water—hard in 3 hours.

Cementation of Water-Bearing Strata.   Rapid setting, even at the expense of strength, is sometimes of value,[149] as in the closing of open-

[143] Davis, Watson, *Eng. News Record,* **87**, No. 1, 26 (1921).
[144] *Cement and Eng. News,* **34**, No. 1, 34 (1922).
[145] McCoy, James P. A., U. S. Pat. 1,286,371 (Dec. 3, 1918).
[146] Gilmore, Q. A., "Limes, Hydraulic Cements and Mortars," Van Nostrand, **1874**, p. 97, 98.
[147] Bornträger, H., *J. Soc. Chem. Ind.,* **20**, 477-478 (1901).
[148] Brunner, Mond & Company, Booklet S. S. 232, Northwich, England.
[149] Burke, J. T., U. S. Pat. 1,552,270 (Sept. 1, 1925).

ings against leaking water and in the process of keeping oil out by cementing the wells during drilling; and the control of it by varying the amount of silicate used enables the operator to adapt his cement to the character of the strata to be sealed.[150, 151, 152] Francois [153, 154] devised a technic for the cementation of water-bearing strata in the sinking of mine shafts and other engineering works. He found that by pumping alternately a solution of aluminum sulfate and sodium silicate into sandstone or other porous formation a gelatinous precipitate was produced which under heavy pressure acted like a lubricant and permitted a cement slurry to penetrate more deeply than would otherwise be possible. This process has been extensively used abroad. Its success depends on highly expert manipulation, and pressures up to 180 atmospheres have been used.[155-169]

Wood-Fiber. Another form of concrete in which silicate solutions are used is that of Zuskoski [170] in which sawdust or wood-fiber [171] is treated with silicate solutions and mixed with cement to make a light mass.[172]

[150] Ztakikawa, Jap. Pat. 37,655 (Dec. 14, 1920).

[151] Wilson, Charles, U. S. Pat. 1,547,189 (April 17, 1924).

[152] Winkler, Kaspar, U. S. Pat. 1,519,285 (Dec. 16, 1924); 1,530,533 (Mar. 24, 1925).

[153] Francois, A., U. S. Pat. 1,391,678 (Sept. 27, 1921); U. S. Pat. 1,430,306 (Sept. 26, 1922); "Sinking of Shafts in Mine Pits by Process of Cementing"; "Shaft Sinking and Cementation in Water-bearing Rocks," Liege, Belgium, **1922.**

[154] Francois Cementation Company, Ltd., Bentley Works, Doncaster, England, Booklet.

[155] Sadtler, Bishop, Vail, Symposium, *Trans. Am. Inst. Chem. Eng.,* **19** (1927).

[156] Anon., *Eng. and Mining J.,* **125,** No. 2, 60 (1928).

[157] Potts, Harold Edwin, U. S. Pat. 1,635,500 (July 12, 1927).

[158] Robertson, I., "The Cementation of the Glasgow District Subway Tunnels." Paper prepared by Inst. of Civil Eng.

[159] Dixson, H. O., "Underground Water Difficulties," *Wigan Mining School,* **5** (1923-24).

[160] Hassam, A., and T. T. Mawson, *Ann. Mines, France,* **9,** Ser. 11.

[161] Blandford, T., "The Principles of Cementation," *Colliery Guardian,* **132** (July 16, 1926).

[162] Ball, H. Standish, *Trans. South Wales Inst. of Eng.,* **36,** 509-74 (1921).

[163] Marriott, Hugh F., "The Francois Cementation Process," etc. Lecture delivered before the Birmingham University Mining Society (May 20, 1919).

[164] Morgan, F. L., "Cementation Methods of Dealing with Underground Water Problems." Lecture delivered before the Birmingham University Mining Society (Feb. 10, 1921).

[165] Robertson, E. H., *Trans. Mining Geol. Inst. of India,* **11,** 144-160 (1916).

[166] Mitton, H. Eustace, *Trans. Inst. Mining Eng. (London),* **70,** pt. 5, 345-367 (1925-26). Paper read before Inst. of Midland Eng. (England), (Oct. 15, 1921).

[167] Hassam, A., and T. T. Mawson, *Trans. Inst. Midland Eng.* (England), **58.** "Sinking a Shaft by the Francois Cementation Process."

[168] "The Francois Cementation Process," *S. African Mining Eng. J.* (June 9, 1923).

[169] *Colliery Eng.,* **1,** No. 6, 270-282 (1924).

[170] U. S. Pat. 1,471,876 (March 8, 1922).

[171] Kelly, Thomas Daniel, U. S. Pat. 1,262,512 (April 9, 1918).

[172] Wheeler, W. H., U. S. Pat. 1,201,535 (Oct. 17, 1916).

Patching Concrete.   Silicate solutions are also an aid in patching concrete; the surface to be repaired is cleaned, painted with a thick layer of syrupy $Na_2O, 3.3SiO_2$, and dusted while still wet with dry cement powder.   This sets within a few minutes and provides a surface to which new concrete binds firmly.[173]

Iron Reinforcing Bars.   A highly alkaline type of silicate has been proposed as a means of providing the alkalinity needed to inhibit rusting at the surface of concrete reinforcing bars.   The silicate solution is applied to the rods and caused to set by dusting with dry Portland cement as in patching, but $Na_2O, 1.5SiO_2$ is chosen.   The iron is dipped in a sticky 45° Baumé solution of the silicate, drained, and dusted with cement powder.[174]   This binds well to the concrete and a safe alkalinity at the surface of the metal, which according to Toch,[175] is all that is needed to prevent corrosion, is assured.

Mechanism of the Reaction.   It cannot be positively stated whether the reaction between Portland cement and silicate solutions is primarily a reaction with calcium silicates.   Free calcium hydroxide reacts quickly with the more silicious silicates and more slowly with the highly alkaline.   This is also the case with Portland cement.   On the other hand, old concrete in which free lime may be assumed to be absent has the property of forming water-resisting masses with silicious sodium silicates.   Probably both reactions occur,—those with free lime much more rapidly than those with calcium or aluminum silicates.

Portland cement added in small quantities to masses in which the primary binder is sodium silicate serves the purpose of giving early

TABLE 75.   *Typical formulas Used to Hasten Set or Increase Resistance to Water.*

30 parts wood flour or residue from corn cobs
30 parts $Na_2O, 2.06SiO_2$
30 parts Portland cement
10 parts water

29 parts graphite
29 parts $Na_2O, 2.06SiO_2$
28 parts Portland cement
14 parts water

72 parts talc
 7 parts $Na_2O, 2.06SiO_2$
 7 parts Portland cement
14 parts water

62 parts whiting
33 parts silicate, ratio 1 : 2.92, 1 : 2.47, or 1 : 2.06.
 5 parts Portland cement

[173] Sterne, E. T., personal communication.
[174] *"Silicate P's & Q's,"* Philadelphia Quartz Company, **5**, No. 4 (1925).
[175] Toch, Maximilian, *Ind. Eng. Chem.*, **15**, 665-666 (1923).

resistance to water and also of taking up water which would otherwise have to be removed by drying.

Other reacting substances can be used to make cements which resist water.

Acid-Resisting Brick Work. Portland cement and silicates of soda have been extensively used for setting acid-resisting brick work in digester linings for the sulfite process of making paper pulp from wood.[176, 177] The iron shell is usually separated from the first course of brick by a one or two inch backing of cement made from sand, Portland cement, clay, and a silicate solution. This is proportioned as follows:

> 1 part quartz
> 1 part fire clay
> 2 parts cement

made up with a silicate solution of such ratio and concentration that it takes a preliminary set in half-an-hour or less. The amount needed will change with the temperature and with the ratio of the silicate solution. $Na_2O, 3.3SiO_2$, $Na_2O, 2SiO_2$, and $Na_2O, 2.5SiO_2$ are frequently used in this country, the last most often. The bricks are set in a cement which contains more silicate and sets as fast as can be worked. The second or interior course is laid with great care, sometimes in a silicate-Portland cement mixture which is afterward pointed with a glycerin-litharge cement, though sometimes the bricks are laid in the more costly litharge composition. The resistance of this is also improved by the addition of small amounts of silicate, which affect its time of set. If $Na_2O, 2.5SiO_2$ be used at specific gravity 1.26 (30° Baumé), the speed of set will increase as the glycerin is reduced. To state it the other way, the silicate and litharge (PbO) react promptly when mixed, and more slowly as the action is modified by introducing glycerin. The amount of litharge, within the limits imposed by a consistency suitable for applying with a knife or trowel, has little influence on the setting time, though the stiffer mixtures tend to set slightly faster.

TABLE 76. *Effect of Silicate on Setting Time of Glycerin-Litharge Cements.*

$Na_2O, 2.5SiO_2$ at 30° Baumé Parts by Weight	Glycerin Parts by Weight	PbO Parts by Weight	
4	0	8	firm in 3 minutes
4	1	8	firm in 3 minutes
4	2	8	firm in 6 minutes
4	3	8	firm in 10 minutes
4	4	8	firm in 25 minutes

[176] Heijne, Otto, *Paper Trade J.,* **80**, No. 23, 61 (June 4, 1925).
[177] Ekstrom, P. G., U. S. Pat. 1,456,303 (May 22, 1923).

Increase in concentration of the silicate will also increase somewhat the reaction time. These compositions resist for long periods the hot calcium bisulfite liquors and such abrasion as results from the circulation of the pulp. They adhere strongly to brick, but care must be used to apply them when they are still thin enough to wet the surfaces and no piece of brick must be moved after initial setting has occurred. This involves mixing small batches at the point where they are to be used. The best plan is to have one worker laying brick, and beside him, another doing the mixing in lots only enough to set two or three pieces.

METALLIC CEMENTS.

Compositions for the repair of metal pieces may be made by mixing silicate solutions with metallic powders.[178] Zinc and aluminum powders react sufficiently with $Na_2O, 3.3SiO_2$ to attain a fair resistance to water after a few days. Such cements when dry will take a polish and are thus suitable for closing defects in castings where the mechanical requirements are not severe.

Gas and water-tight repairs to engine cylinders and the like are made with cements of this type. Silicates of soda and iron filings are rarely used, as the silicate covering prevents the rusting of the iron which is desirable to expand and harden an iron cement. When the repair is made on iron, the silicate cement adheres best to a rusty surface or one that has been scaled slightly by heat. Silicate cements from soapstone or other earthy materials which are not hydrous give good service on hot iron.[179]

SATURATION WITH SILICATE SOLUTIONS.

Structural Stone. Kuhlmann applied diluted silicate solutions to marble statuary, plaster, brick, concrete and structural stone for the purpose of hardening them and decreasing their tendency to disintegrate with age. His expectations have not stood the test of time. It is a matter of some difficulty to obtain penetration of a dense body with a silicate solution which, when spread upon a surface of very fine porosity, undergoes a partial dialysis, with a tendency to leave most of the silica near the surface. While this is most clearly observed by attempting to saturate a piece of hard wood, it must also play a part in the treatment of most natural stone in place. It is extremely unlikely that Kuhlmann was able to surround every particle of the stones he treated

[178] West, Frank P., U. S. Pat. 1,388,011 (Aug. 16, 1921).
[179] Dunnington, F. P., personal communication.

with a silicate solution or a gel. If he could not do this the weathering of the stone would proceed by the decay of the untreated portions, even though the treated parts were perfectly protected. With or without the use of precipitating agents such as calcium chloride, no permanent results were obtained.[180, 181]

According to Gilmore,[182] "There is a variety of other important uses to which this silicifying process, as it may be termed, can be advantageously applied, for our knowledge of which we are chiefly indebted to Kuhlmann, Professor of Chemistry at Lille, and Fuchs. We will refer to them very briefly in this connection.

"When a solid body, of any degree of porosity, is immersed in water or any other fluid, it rapidly absorbs a certain quantity of the latter, until the point of complete saturation is reached; and if, in addition, the fluid possesses reacting powers, certain chemical changes will ensue within the pores of the solid body. If a porous limestone, like chalk, for example, or a piece of mortar of fat lime, be dipped in a solution of alkaline silicate, a certain portion of the silica in solution, after its absorption, will part with its potash or soda, and enter into combination with the lime, whilst another portion will remain mechanically interposed in the pores of the solid body, and will, in time, if exposed to a current of air, solidify by desiccation. The result will be that, with a single immersion, the density and hardness of the chalk or the mortar will be augmented, and after several alternate immersions and exposures to the air, these properties are attained in a considerable degree. The softest varieties of chalk may be thus hardened, so as to become capable of receiving a high polish.

"Upon the sulfate of lime or plaster, the action of the alkaline silicate is essentially the same, though more rapid, and is accompanied by the inconvenience of giving rise to an alkaline sulfate, which, in crystallizing within the pores of the solid body, near the surface, is apt to cause disintegration. It is recommended in this case to use the solution more diluted, with a view to retard or diminish the effects of the crystallization of the sulfate, to such a degree that the indurating solid will be able to resist it.

"The process of silicatization, so named by Kuhlmann, which rests upon the principles enunciated above, is of undoubted utility, although, as yet, its practical application is attended with difficulties, and followed, not unfrequently, with uncertain results. It appears destined

[180] *Deut. Bauzeitung*, No. 48 (1868) ; Abst. *Chem. Zentr.*, **40**, 816 (1869).
[181] Olfers, *Poly. J.*, **176**, 229 (1865) ; Abst. in *Chem. Zentr.*, **36**, 656.
[182] Gilmore, Q. A., "Limes, Hydraulic Cements, and Mortars," New York: D. Van Nostrand & Co., **1874**, p. 98-99.

to meet with a varied and extensive application, in the industrial and fine arts, not only in the conversion, at a moderate cost, of common into hydraulic lime of any required degree of activity, and with a fair, or at least, encouraging degree of strength, but in the preservation of walls of whatever kind, already constructed unadvisedly of materials liable to more than ordinarily rapid decay, whether of brick, stone, pisé, or concrete; in the restoration and conservation of statuary, monuments, architectural ornaments, etc.; in transforming designs cast in ordinary plaster into hard and durable stone; in rendering wood-work; and, to a limited extent, even cloth fabrics indestructible by fire; and in a multitude of other collateral uses, some of which are even now well developed and in practical operation, while others remain still in their infancy, giving more or less encouraging promises of future utility and value."

Water and Oil-Resistant Concrete. Portland cement concrete differs from sandstone or even marble in two important respects. It is chemically more reactive toward the silicate solutions, and the silicate treatments which are applied to its surface are directed to decrease its permeability and to increase its resistance to abrasion rather than to alter the erosion effects of the elements. Its pore structure is often such that a silicate solution will penetrate for several inches.[183]

Most cement bodies are more or less porous. This is particularly true of Portland cement concretes which set by a process of crystallization or hydration of insoluble silicates. One method of closing the pores consists in applying a silicate solution sufficiently dilute to penetrate and sufficiently unstable to deposit a gel in the capillary openings. If the concrete is fresh enough to contain some free calcium hydroxide a satisfactory reaction may be had with a 10 per cent solution of $Na_2O, 3.25SiO_2$. The preferred method of treatment is to saturate the cement with the silicate on three successive days, which is usually sufficient to seal the cement so that it will absorb no more. If this is not the case, other saturating treatments may follow. A gel, being a permeable substance, can never produce water-resistance such as may be expected from oily or asphaltic layers, and aside from its essential permeability there is probably some separation from the cell walls by syneresis. Nevertheless, substantial improvements in water-resistance can be made by silicate as indicated in the following graph, from which it may be seen that the treated test piece absorbed about half as much water as the untreated when both were subject to a thirty-foot head

[183] "Stone Preservation Committee Report, Dept. of Sci. & Ind. Research," London: His Majesty's Stationery Office, **1927**, p. 22.

and that while water flowed steadily through the untreated piece there was no flow through that which had been treated.

If the cement is so old that all the free calcium oxide has been converted to calcium carbonate, the silicate will require longer to develop maximum resistance to water and may not become entirely insoluble until it has absorbed enough carbon dioxide from the air to cause the gelation of the silica.

When the substance in the pores is only a dried silicate solution the resistance to oils is very high, for dried silicates are glass-like bodies and resist admirably liquids which do not dissolve them. Free fatty acids may be partly saponified if the silicate in the pores has not been sufficiently dried, but no reaction
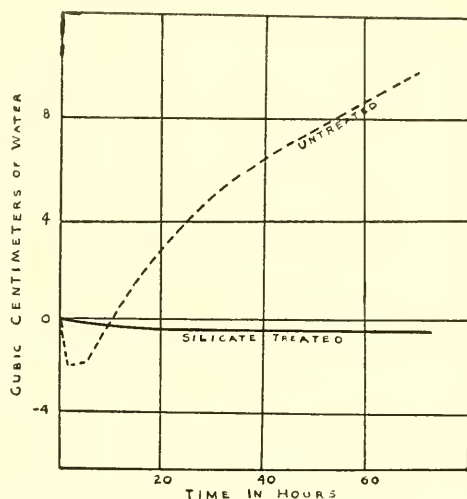
FIG. 87.—Penetration of Water into Concrete with and without Silicate Treatment. (Courtesy Brunner, Mond & Co.)

TABLE 77. *Tensile Tests on 1:3 Mortar Briquets.*

(Brunner Mond and Company)

Ultimate Strengths in lbs. per square inch.
(Average of four briquets.)

Days	A	B	C	D	E	F	G	H	I
		Untreated		Standard briquets immersed for 7 days in 5% sod. sil. soln. Stored in damp sand when not immersed.			Standard briquets dipped 3 times at 24-hour intervals in 20% sod. sil. soln. and stored in damp sand.		
7	202	120	270						
21	301	190	419	323	368	350	321	342	359

takes place in the absence of water. Silicate-impregnated concrete is thus an excellent container material for mineral and vegetable oils.[184-188]

[184] Moyer, Albert, *Concrete,* **4**, 49 (1910) ; *Can. Eng.,* **19**, 707 (1910) ; *Concrete,* **16**, 279 (1920) ; *Concrete Cement Age,* **4**, 135 (1914) ; *Eng. Record,* **62**, 624 (1910) ; *Proc. Am. Soc. Testing Materials,* **10**, 351-355 (1910).

[185] "Report of Service Tests on Concrete Floor Treatments," Bur. of Standards (Oct. 28, **1920**).

[186] "Silicate of Soda and Concrete," Philadelphia Quartz Company, Bulletin No. 34 (1925).

[187] Proc. Am. Road Builders' Assoc., 24th Annual Conv. (Jan. 11-15, **1927**).

[188] Huth, F., *Farbe und Lack,* 606 (**1925**).

Protection against oil penetration is also desirable in factory floors and garages. The application is the same as for water-resistance, but
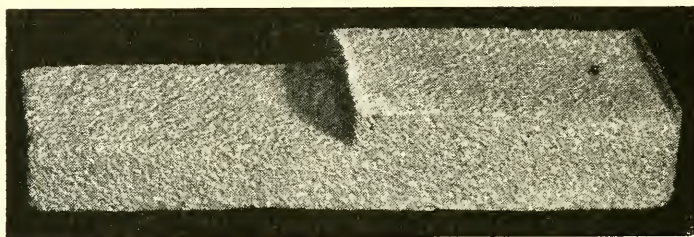
FIG. 88.—Abrasion Test Showing Effect of Silicate Treatment on Concrete.

the contrast in oil absorption before and after treatment is more striking than the results shown above for water.[189]

Concrete Hardening. Silicate treatment of concrete gives it a greatly increased resistance to abrasion. This may be shown by rubbing the test piece with sanded blocks under standardized conditions. The piece shown in the picture was made in this way. The 2 : 1 sand-cement mortar block was silicated for half its length and each end subjected to the same amount of rubbing. The narrow fin indicates the original thickness of the piece where no abrasion was applied, the next step is the silicated part, and the thinnest portion is the original untreated concrete.

Wear on a concrete floor or roadway means a corresponding amount of dust which is inimical to the satisfactory performance of many industrial processes.[190, 191, 192] Saturation with silicate solutions is inexpensive and for many conditions affords a complete solution of the problem.

Curing Concrete.[193] Further use of silicate solutions in connection with Portland cement concrete is in connection with the curing process. If a coating of silicate be applied to the cement as soon as possible after the initial set, that is, when it is hard enough to bear the weight of a man without marking, the water escapes less readily than it would without the silicate treatment and there is some evidence that the final strength of the concrete is improved.

Advantages claimed for this method of curing are the ease and cheapness at which it may be applied, the fact that no labor is required for removing the curing medium, as in the case of earth or straw, and its

[189] Dulac, A., Brit. Pat. 250,439 (July 14, 1925) ; *C. A.*, **21**, 1174.
[190] Stubbs, Robert C., U. S. Pat. 1,315,749 (Sept. 9, 1919).
[191] Brunner, Mond & Co., *Dyer, Calico Printer* (Aug. 15, 1924).
[192] Remler, R. F., *Fibre Containers*, **11**, No. 2, 16 (1926).
[193] Beightler, Robert S., *Eng. News Record,* **100**, 316 (1928).
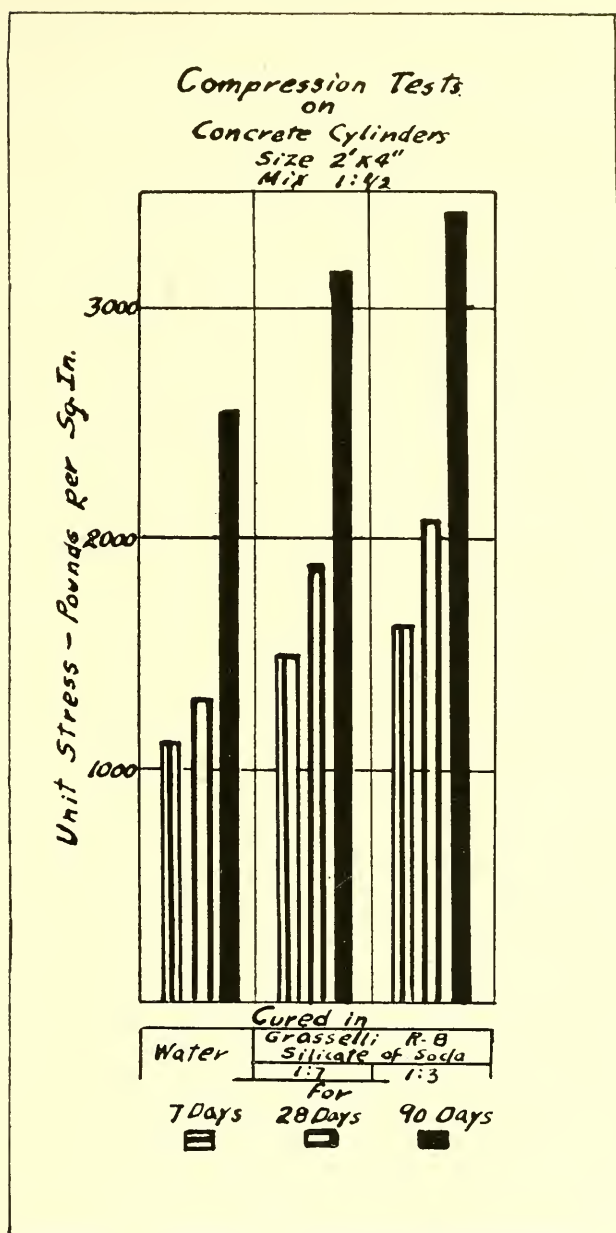
Compression Tests on Concrete Cylinders

FIG. 89.

adaptability to localities where water is not plentiful. Ball indentation tests and compression and loading tests of beams indicate that at least under optimum conditions the silicate curing treatment will increase the strength of concrete.[194]

Another means of indicating the effect of silicate treatment on wear

[194] Remler, *loc. cit.*
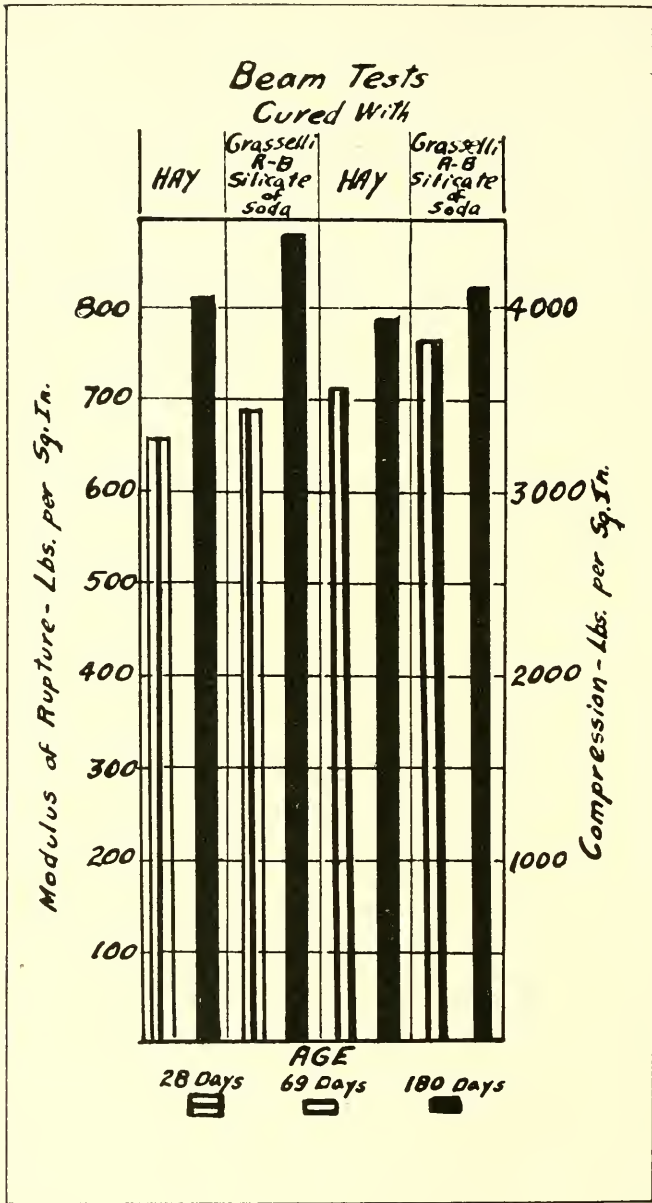
Modulus of Rupture and Compression Tests on Concrete Beams

FIG. 90.

is to apply the Continental method of observing the depth of penetration of a sand blast applied to the surface. The following graph from Otzen [195] indicates that whether the silicating is done early or late there is always a striking contrast between the raw and treated pieces.

[195] Otzen, Robert, personal communication, Tech. Hochschule, Hannover (Nov. 19, 1924).

TABLE 78. *Surface Hardness Test.*

Size of beams	40″ x 6″ x 8″
Mix	1–1¾–3½
Hay cured	14 days
Age when tested	60 days

Indentation Loads, Pounds.

Silicate of soda treated	10,465
Untreated	8,915
Difference	1,550

These data are averages of 25 to 30 determinations.

Indentation load is the pressure necessary to force a one-half inch steel ball one-quarter inch into the concrete surface.
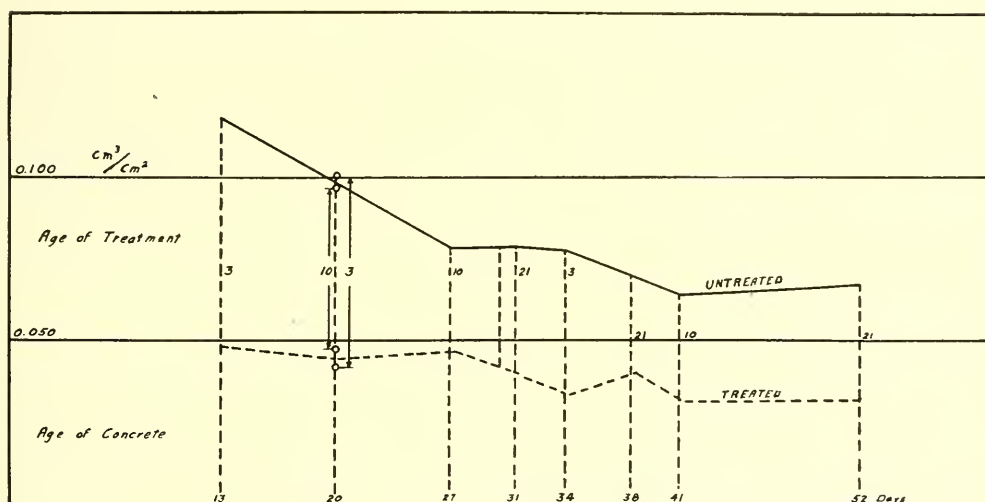
FIG. 91.—Sand Blast Penetration of Concrete with and without Silicate Treatment.

The frequency with which it is desirable to repeat silicate treatments will to some extent depend upon the amount of traffic. A factory floor subject to iron-wheeled truck traffic may need a fresh saturation every six months, while many lighter services need it only once.

Acid-Resistance. More frequent still is the need of repeating the silicating where floors are subject to the action of weak acids. Concrete does not resist strong mineral acids, and silicate treatment is not sufficient protection to warrant designing floors for exposures of this sort though silicate has done good service when old floors had to be used and ideal conditions could not be met. Concrete floors have been successfully protected against large amounts of weak organic acids by silicating at relatively short intervals—in some cases weekly.

Chapter VIII.

Adhesives.

Definition and General Behavior.

Adhesive substances have had important uses from very early times. Solutions of starches, glues, and gums, drying oils, and other colloidal substances have been used to cause the adherence of paper, wood, light metals, ceramic wares, and objects for decoration or use in all the arts. The science by which we shall understand their performance has lagged behind the art of putting them to use. Before considering specifically the function of soluble silicates as agglutinants it may be worth while to set down a few points of general application.

Adherence and Coherence.

Webster contrasts the ideas of adherence and coherence by citing the difficulty of separating a pile of smooth glass plates, which cohere with great tenacity. Metals or other dense materials with perfectly fitting surfaces exhibit the same phenomenon. His distinction between the holding together of two like surfaces such as glass or metal and two different substances as wood and glue serves for most of the instances with which we are concerned. Adhesives are different from the surfaces on which they are spread.

Film Formation.

To perform their office of uniting, they must be able to wet the surface and form a more or less continuous film. The strength of the union produced will be a function of the strength of the film which lies between the surfaces to be bound. Adhesives take their grip either by specific adsorption or by penetrating surfaces more or less rough or porous and by forming protrusions on the film which in the course of the process changes from a fluid to a relatively solid condition.

The materials which fill these requirements are usually concentrated viscous liquids which do not tend to crystallize at ordinary temperatures and that among the soluble silicates there are numerous materials fitted to act as adhesives.

GENERAL CHARACTERISTICS OF ADHESIVES.

Although its first report did not deal at all with these mineral adhesives, the Adhesives Research Committee [1] has set forth some considerations applicable to all adhesive materials as well as to animal glues, which they investigated.

"Glues are most commonly employed for sticking together surfaces of wood; these are relatively rough and uneven, and no matter how closely a pair of wood surfaces be pressed together, the actual points of contact form probably but a fraction of the area of overlap. Between the points of contact are relatively large air spaces. In well-glued joints, the glue not only covers the portions of the two pieces of wood which touch, but it fills in the spaces which would otherwise be occupied by air. In this way, only, can a strong rigid structure be obtained. Glass surfaces can be ground to such an accuracy that they fit each other perfectly. Not so wood surfaces, where the interspaces must be filled with an adhesive. For this purpose, an adhesive must obviously be, at time of application, a viscous liquid, since a mobile one could not be retained in place, as it were, until the joint was made.

"If, however, glue is too viscous it will not readily fill the interspaces, and the joint is consequently weakened. Thus, for each class of material to be glued there is possible an optimum viscosity dependent upon size of interspaces and pores of that particular material. This may be one underlying reason for a characteristic feature of the glue industry, i.e., the selection of numerous special glues for specific purposes.

"Adhesives, then, must be viscous substances; since viscosity is generally connected with high molecular weight, or at least with high molecular association, they are usually substances of complex chemical composition."

The close analogy between the adhesive characteristics of animal glues and silicate adhesives is readily seen.[2, 3, 4]

An extended systematic study of adhesives and adhesive action by McBain[5] and Hopkins led to the conclusion that adhesive joints are of two types, namely: specific and mechanical. The first are formed between smooth, non-porous surfaces and are probably associated with

[1] "First Report of Adhesives Research Committee," Dept. Sci. and Ind. Research, London: His Majesty's Stationery Office, **1922**.

[2] "Second Report of Adhesives Research Committee," Dept. Sci. and Ind. Research, London: His Majesty's Stationery Office, **1926**.

[3] *J. Phys. Chem.*, **29**, 188-204 (1925).

[4] *J. Phys. Chem.*, **30**, 114-125 (1926).

[5] McBain and Hopkins, Second Report of Adhesives Research Committee, London: His Majesty's Stationery Office, **1922**, p. 34. See also McBain, J. W., and W. B. Lee, *Ind. Eng. Chem.*, **19**, No. 9, 1005 (1927).

adsorption phenomena. The latter can be formed by any liquid which penetrates porous surfaces and then becomes solid *in situ* as by cooling, evaporation, oxidation or otherwise. Such joints depend largely for
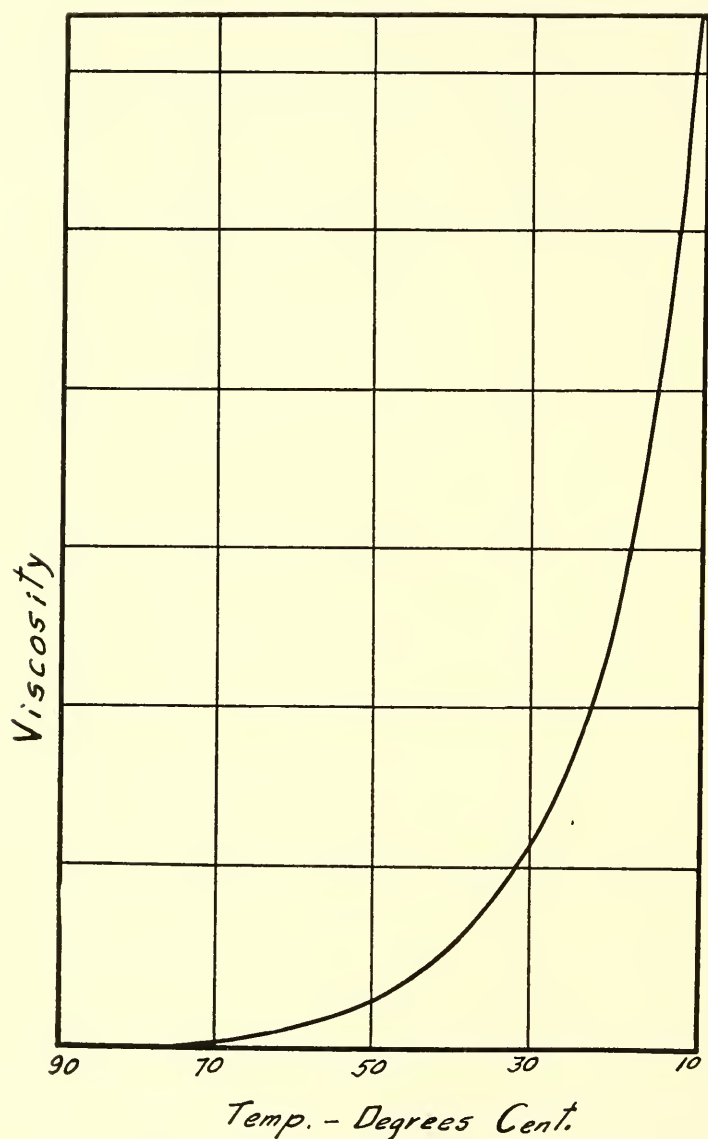
Fig. 92.—Relation of Viscosity to Temperature for $Na_2O, 3.34SiO_2$ (43° Baumé).

their strength upon the strength of the adhesive itself, for they are essentially cases of embedding the substances to be stuck in the adhesive which forms a link that must of itself carry any load placed on the system. Specific joints on the other hand may be much stronger than the adhesive as in the case of a soft shellac which made joints between metals many times stronger than its film strength (nearly two tons per

square inch).   The combination of specific and mechanical adhesions may often occur.   In general, any liquid which wets a surface and is then transformed into a solid may be regarded as an adhesive for that surface.
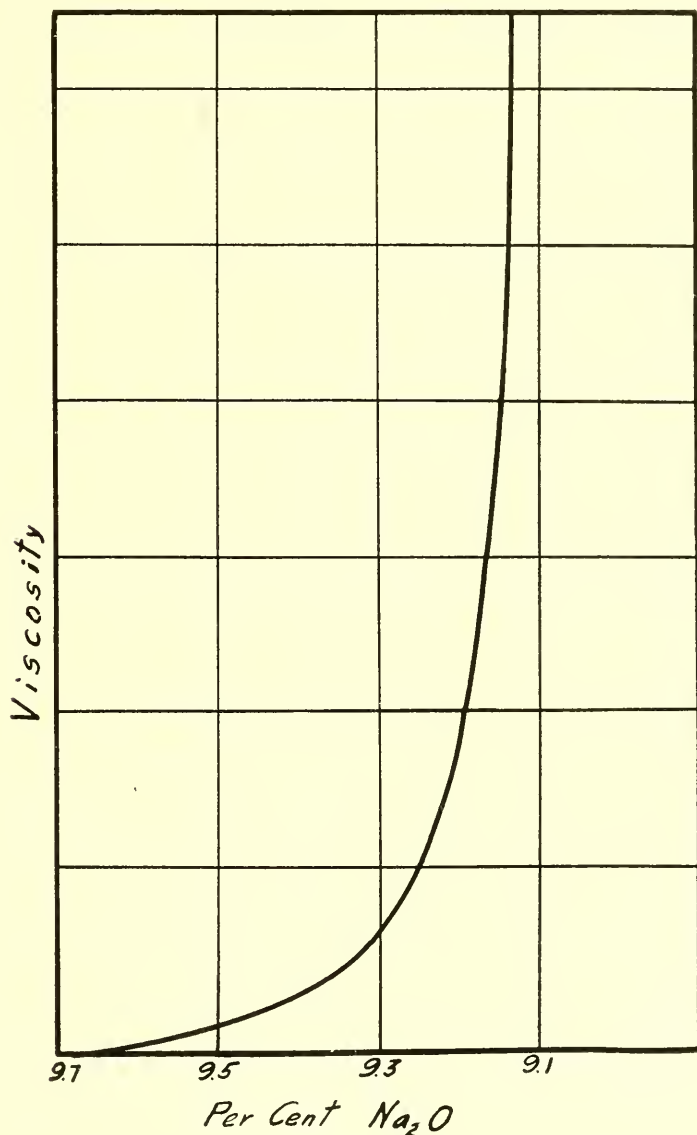
FIG. 93.—Relation of Viscosity to Alkalinity for $Na_2O, 3.34SiO_2$ (43° Baumé).

SET AND VISCOSITY.

The porosity of the surfaces to be attached will determine the viscosity required at a given pressure—more pressure may cause too great a penetration which is conveniently resisted by a greater viscosity. If there were no other variable the ideal pressure-viscosity relation could

be easily worked out for each particular surface with a given adhesive. But an adhesive must set, that is, the liquid must become solid—its
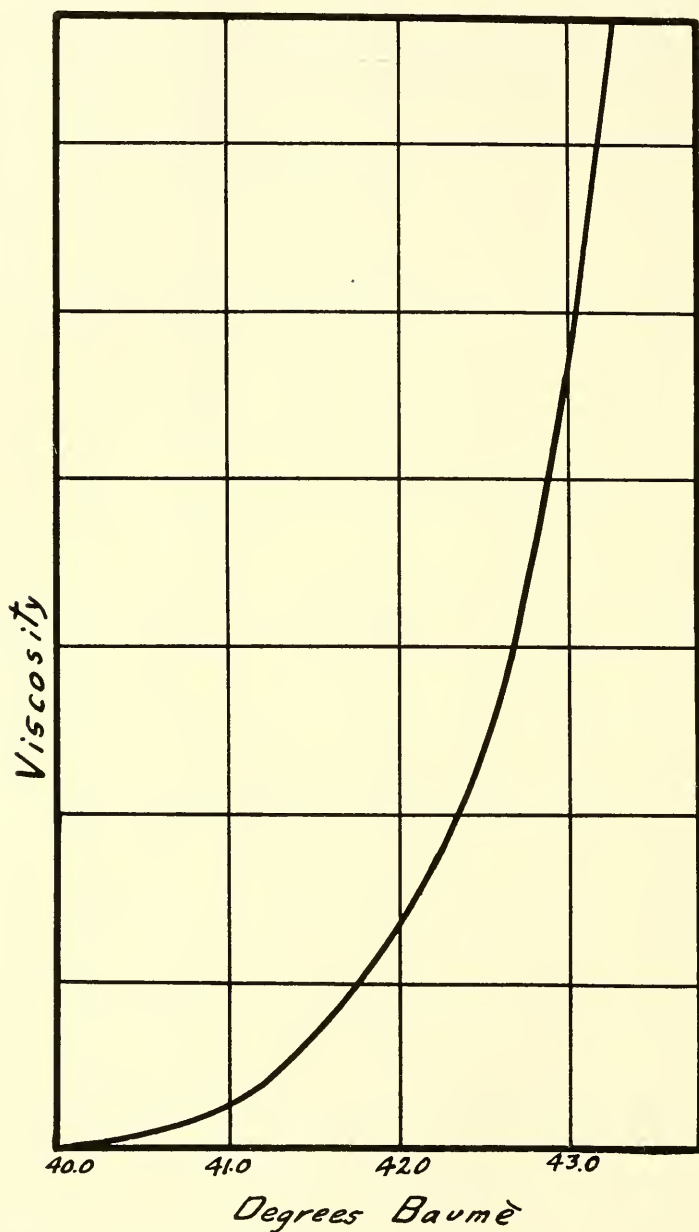
Fig. 94.—Relation of Viscosity to Specific Gravity for $Na_2O, 3.34SiO_2$ at Constant Temperature (20° C.).

viscosity must rise. This usually begins as soon as it becomes a film. Thus the time element enters. This is variable for each adhesive liquid and for each surface. It is usually a vital consideration in industrial processes.

If the setting of the adhesive depends upon the transfer of moisture from the adhesive to the surface stuck this will primarily relate to the area which functions as an absorbent. It follows that thick films will set more slowly than thin ones; the amounts of water removed, though the same per unit of area, are different proportions of the large and small quantities of adhesive.

The ability of surfaces to absorb will vary not only with porosity but with the amount of water already present. Wood or paper, being sensitive to the fluctuations of atmospheric humidity, will vary the setting time of aqueous adhesives.

Typical graphs for the viscosity rise of silicate solutions beginning with the type $Na_2O, 3.3SiO_2$ (Figs. 92, 93, 94) show that the curves of increases due to cooling, to reduction in relative alkalinity, and to concentration are of nearly the same shape, but it should here be pointed out that air drying never completely removes moisture. The solid film is really a highly concentrated silicate solution containing 20 per cent of water, more or less, and capable of becoming somewhat fluid when quickly heated to temperatures near the boiling point of water. The tendency to liquefy may be offset by evaporation. The water-containing film is, like the hydrous silicate powders of commerce, capable of being dissolved by hot water. It must be modified if completely insoluble adhesives are desired.

Choice.

The conditions which the finished work is required to withstand will have much to do with the selection of an adhesive. Must it resist water? How quickly must the bond be formed? How long must it endure? Is an alkaline adhesive permissible? What is the cost? These are all questions which must be answered before an adhesive can be wisely chosen. There are many more, but these will serve to indicate the difficulty of reducing all the variables to measurable units and of making and choosing adhesive compositions by cut-and-try methods.

Silicate Adhesives Unmodified by Other Materials.

Silicate solutions may be used either alone or mixed with modifying substances for adhesive purposes. We shall consider first the use of solutions containing only water, Na_2O, and SiO_2 on sundry surfaces.

Glass.

Bottles on which syrupy silicate solutions between $Na_2O,2SiO_2$ and $Na_2O,4SiO_2$ have been spilled will often adhere to each other or to

wood or stone shelving with such tenacity that it is impossible to salvage them. The grip of silicate solutions on glass surfaces is partly due to a slight etching of the glass which at the same time tends to disturb the equilibrium between silica and soda, increase the viscosity, and produce a more water-resistant film than would be formed on an inert surface.[6] $Na_2O, 2.7SiO_2$ is often sold in small bottles for the repair of china and glassware. The joints when freshly made will not stand long immersion in water but become better as the reaction proceeds slowly over the course of years. Large surfaces of glass give difficulty from slow setting, for evaporation takes place only at the edges. The reaction with ordinary flint glass and a 1.41 specific gravity (42° Baumé) solution of $Na_2O, 2.7SiO_2$ is sufficient to cause gelation in about two years at atmospheric temperature in a sealed test tube. The same liquid stored in iron would show no measurable change in viscosity in that time. Silicate solutions have been mistakenly used to fasten temporary signs on polished plate glass windows. They are very difficult to remove completely. The best method is to apply acetic acid followed by hot water and then restore the original polish with fine abrasives and rouge. McBain gives the following tension tests of a series of silicate solutions on glass:

TABLE 79. *Tension Tests—Silicate Adhesive between Glass Surfaces.*

Grade of Silicate	Single Coating Lbs. per Sq. In.	Double Coating Lbs. per Sq. In.
Grade 5 molar ratio 2.0	...*†	...†
" 1 " " 2.45	300	200
" 2 " " 2.9	1,000	500
" 3 " " 3.0	600	800
" 4 " " 3.3	600	800
Experimental sample 4.08	567‡	600

* Film moist.
† No test possible as the joints were too weak to withstand ordinary handling.
‡ Maximum values.

These results are inconclusive in the absence of information that optimum concentrations, viscosities, and drying times were used.

MICA.

Heat-resisting translucent sheets are built up by dipping thin pieces of mica in silicate solutions rather thinner than is usually chosen for glass and laying them together upon a support until a sheet of the desired size and thickness has been formed. It is then pressed and baked. $Na_2O, 2.4SiO_2$ does this satisfactorily. There is probably some

[6] Norman, John Thompson, U. S. Pat. 949,493 (Feb. 15, 1910).

reaction with the mineral. When these sheets are kept dry their electrical insulating properties are good; when moist, the insulating properties are much reduced and some efflorescence of the exposed silicate films is to be expected.

Asbestos Paper.

Adjustment of Viscosity. Mineral fibers have for many years been made into paper because of their heat-resisting qualities. Parkyn [7] proposes to use asbestos board for wall board. When asbestos paper is to be adhesively united the advantage of a mineral and incombustible adhesive is obvious. Asbestos paper is normally very porous. When dry it is white in color and pleasing to the eye, but water causes it to assume while wet a dark greenish gray color. Silicate solutions thin enough to penetrate the paper also cause this color, which remains after the silicate has dried to a solid condition, though it will not be entirely dehydrated. In order to make a silicate adhesive which will not discolor asbestos paper, it is necessary to adjust the viscosity to a point where wetting is at a minimum. Sulzberger [8] used silicate to render asbestos paper translucent for copying and transfer purposes.
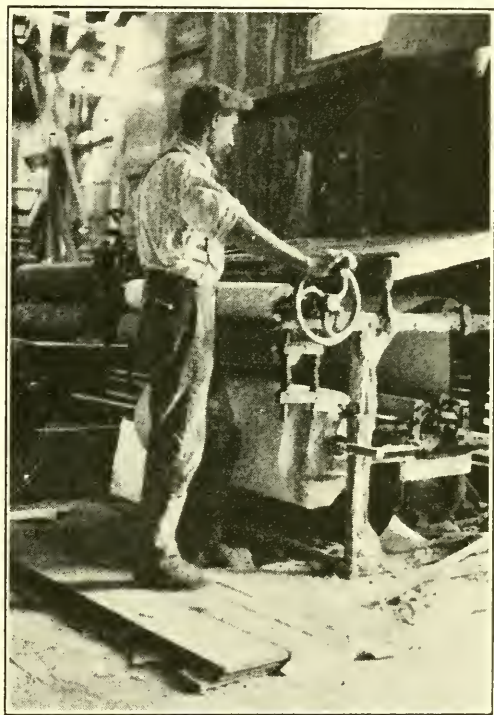
Fig. 95.—Making Asbestos Air Cell Covering, Hand Method.

Corrugated Paper. Corrugated asbestos paper is made into air cell covering for thermal insulation of steam pipes and other conductors, or containers for both hot and cold fluids.

In corrugating asbestos paper the pressure of the toothed roll carrying the wavy member to the tips of which the silicate has been applied would be great enough to drive the adhesive too far into the porous paper. This may be overcome by lightly coating the surfaces which will be inside with a diluted silicate solution which serves to stiffen the sheet

[7] Parkyn, Herbert A., U. S. Pat. 1,466,246 (Aug. 28, 1923).
[8] Sulzberger, Nathan, U. S. Pat. 1,597,301 (Aug. 24, 1926).

and at the same time reduce the penetration of the adhesive. This sizing silicate should be dried by drawing over a heated surface before the adhesive is put on.

Mill Board. Sheets of asbestos paper dipped in silicates thin enough to penetrate them may be pressed together to form a rigid mill board of any desired thickness. The composition ordinarily used as an adhesive for asbestos is $Na_2O, 3.3SiO_2$. Although there is probably some reactions (*cf.* asbestos and silicate in cements, p. 191) these masses are not completely resistant to water. Mill boards have, however, appeared on the market in which a surface treatment with Portland cement has been relied on to make them insoluble. Katz[9] made asbestos products
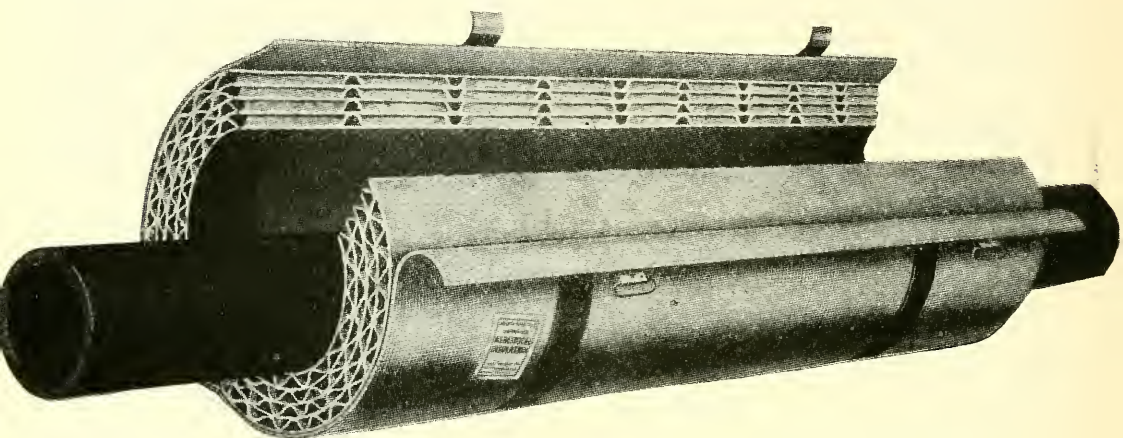
FIG. 96.—Asbestos Air Cell Covering.
(Courtesy, Johns Mansville Corp.)

with good water-resistance by adding calcium carbonate as a filler to the asbestos paper and then saturating it with $Na_2O,2SiO_2$, which reacts relatively rapidly to form an insoluble silicate. The by-product calcium carbonate which results from the treatment of dolomitic limestone to separate magnesia, is especially useful because its reaction with the silicate is somewhat increased by the presence of small amounts of magnesium hydroxide.

TABLE 80. *Typical Analysis of By-Product Calcium Carbonate.*

	Per Cent
Loss on ignition below redness......................	6.98
Total loss on ignition.............................	46.9
Insoluble in HCl	.27
MgO in water soluble form.........................	.46
MgO in water insoluble form.......................	2.72
CaO in water insoluble form.......................	44.25
Al_2O_3 and Fe_2O_3...................................	3.76
	98.36

[9] Katz, Henry G., personal communication.

Pipe Covering. Creped asbestos paper has been made into pipe covering by spotting it with a viscous silicate solution as it was being rolled into the desired form. Thus the insulating value was retained without too greatly increasing the weight or rendering the completed structure brittle.
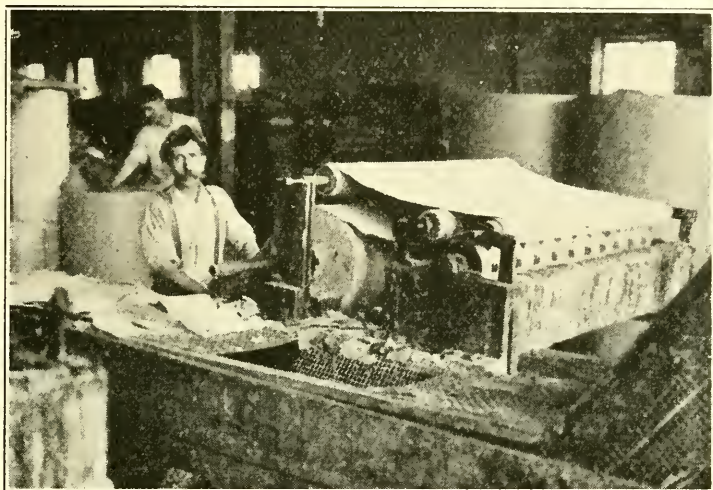
Fig. 97.—Creped Asbestos Paper Made into Pipe Covering by Spotting with Silicate Solution.

Wood.

Shearing Strength. Shear tests of silicate joints between walnut surfaces indicate the greatest strength with ratio 1 : 3. The experiments on which the chart (Fig. 98) is based took no account of viscosity relations but used commercial solutions as received.[10] Work done in McBain's laboratory indicates that higher values can be secured by adjusting viscosity. It is noteworthy that a silicate of approximately the optimum composition was chosen by cut-and-try methods and made standard for most adhesive uses of silicate in the wood and paper industry long before any strength measurements were made.

Dove Tail Boxes. Silicate adhesives on wood have been extensively used for fastening the dove-tailed corners of small boxes made from sawed lumber. The type $Na_2O, 3.3SiO_2$ is almost exclusively used. Its solutions are sufficiently alkaline to give a yellow color to the outside surface. Economy demands that the dove-tailed ends be dipped in the silicate before fitting.

[10] McBain and Hopkins, *loc. cit.,* "Second Report of Adhesives Research Committee," London: His Majesty's Stationery Office, **1922**, p. 43.

Plywood.   Plywood for temporary service, especially that from soft wood, as gum and poplar, when water-resistance is not required, may be made with a silicate adhesive.   The strength of bond is ample for such purposes as shipping boxes for textiles, of which many have been used.[11]

Pieces of smooth sawed maple wood fastened together end to end under a pressure of about 4.218 kilos per square centimeter (60 pounds

Fig. 98.—Shear Tests. Silicate of Soda between Walnut Surfaces.

to the square inch) with a 1.41 specific gravity (42° Baumé) solution of Na_2O, $3.3SiO_2$ will develop over night a tensile strength of more than 52.6 kilos per square centimeter (750 pounds per square inch).   It requires only about 14.0 kilos (200 pounds) to pull the fiber sidewise out of gum veneer.

The ordinary procedure is to use a two-roll glue spreader with fluted rolls 20 to 30 cm. (8 to 12 inches) in diameter.   The lower roll dips into

[11] For Nomenclature, specifications, and grades used in this industry see *Paper*, **35**, No. 12, 503 (1925).

the silicate and the depressions cause a larger amount to be carried to
the upper roll than would be the case if it were smooth. For three-ply
rotary-cut veneer the center sheets from 0.127 to 0.32 cm. ($\frac{1}{20}$ to $\frac{1}{8}$
inch) thick are passed between the silicated rolls and coated on both
sides at the rate of 415 to 439 kilograms per 1000 square meters (85 to
90 pounds per 1000 square feet) of surface. This sheet is laid by hands
protected with rubber gloves upon the dry sheet which is to form the
outside of the plywood; the grains of the two pieces are placed at right
angles. Two dry sheets are laid on top and the operation repeated till
perhaps thirty centers have been laid. The pile is then trucked to a press
and enough force put on to flatten the sheets and make a perfect contact.
The pile is clamped in this position and allowed to stand for several
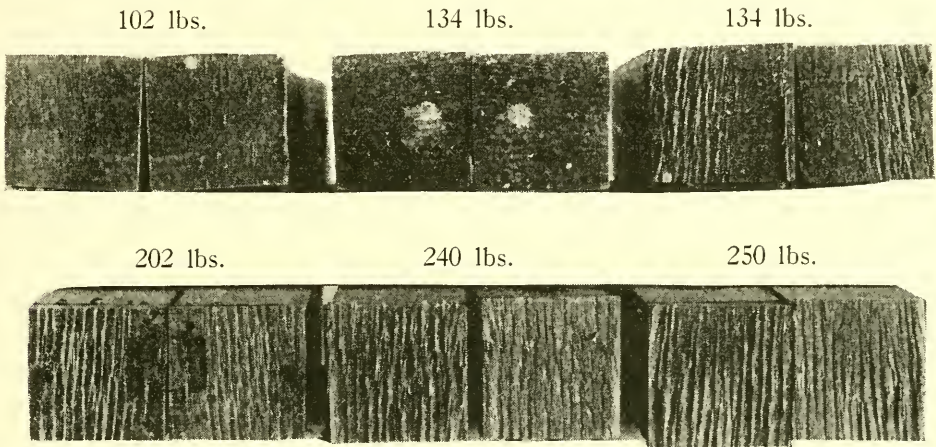
Fig. 99.—Broken Test Pieces Showing the Effect on the Face of Gum Veneer of
Silicate Bonds Ruptured under Various Loads.

hours, preferably over night, when the sheets may be taken out and
sawed.

Pressure should be put on within twenty minutes from the first
spreading of silicate. Larger amounts are needed than if there were
no waiting period, but the dry sheets are not so easily wetted as paper,
and on this account also liberal spreading is necessary.

Silicate adhesives have the great advantage of introducing a minimum
of moisture into the wood. The loss of 20 per cent of the weight of
the silicate, nearly all of which is absorbed by the wood, is enough to
form a bond permitting the laminated stock to be trimmed with saws.
The entire process is accomplished without any special attention to
drying; ordinary handling gives enough ventilation to dry the plywood.

Effect of Age. Though the initial strength is ample and the con-
venience of manufacture great, exposure to water quickly loosens the

bond. Even when the silicate-bound plywood is kept reasonably dry there is enough water normally present in the air-dry silicate (about 20 per cent) and in the wood to permit slow absorption of carbon dioxide and a gradual granulation of the colloidal film. This is often erroneously referred to as crystallization. Observation of commercial processes leads to the general statement that under dry conditions, but without the protection of varnish films or other covering, the silicate holds satisfactorily for one to two years on plywood, though, as will later appear, its service on paper products is much longer. Carter made a study of the effect of age, using dense maple blocks glued end to end, and obtained the following data:
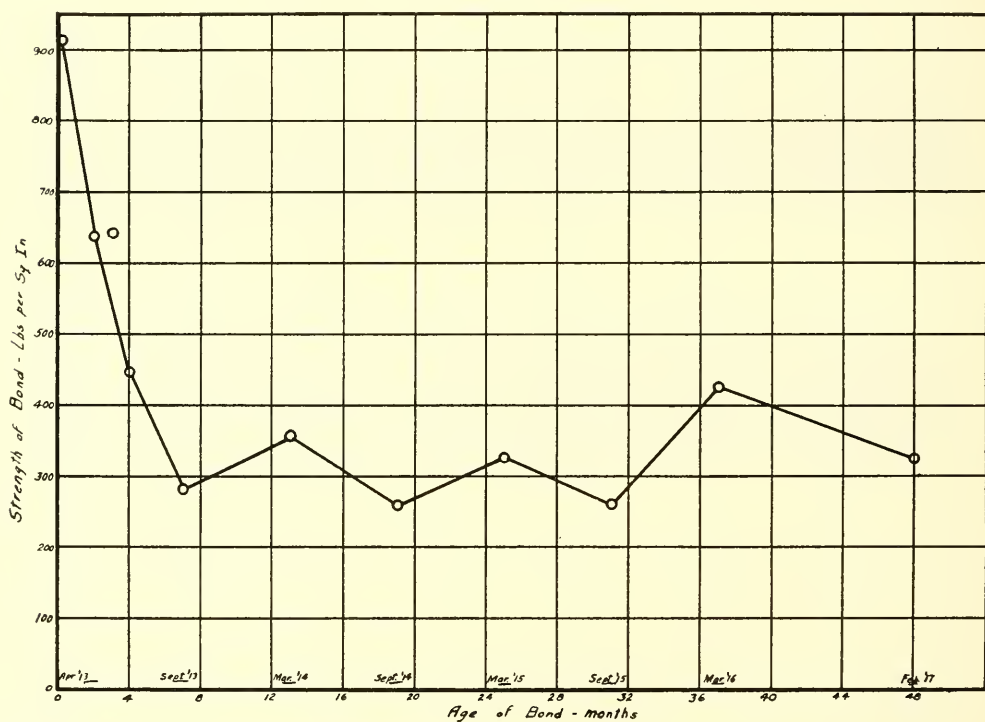
Fig. 100.—Effect of Age on Strength of $Na_2O, 3.34SiO_2$ Bond on Maple Wood Pieces 1 Inch Square.

For work which must resist water and endure permanently, silicate serves in various protein adhesive mixtures.

VULCANIZED FIBER.

Many attempts have been made to bind sawdust and other forms of wood or fiber waste with silicate [12] (see Chapter VII). Other materials

[12] Oelhafen, John Walter, U. S. Pat. 1,564,706 (Dec. 8, 1925).

may be attached to wood with silicate adhesives. Here it will suffice to mention the so-called vulcanized fiber, a dense cellulose sheet made by treating paper with zinc chloride solutions until the fibers become gelatinous, pressing and washing. This fiber is adhesively laid upon sawed lumber or plywood to make trunks. Here the life of silicate films is greatly increased because contact with water and carbon dioxide is much reduced by coating the outside with paint and varnish. If the fiber chosen is of good grade and 0.127 cm. ($\frac{1}{20}$ inch) in thickness, and proper precautions are used to dry the silicate film, which must be of low relative alkalinity, the results are quite satisfactory; but porous fiber or inadequate drying may permit the migration of enough alkali to the surface to make an oil varnish sticky.

The ordinary practice is to apply adhesive silicates cold, but it has been found satisfactory to coat the wood rather heavily with silicate and allow it to dry to a glossy film. The fiber is then placed dry on the silicated surface and both are put into a hot press which melts the solid silicate solution and causes it to take firm hold of the fiber and set by the combination of further evaporation and cooling. This has the advantage of requiring less drying and permitting neater working, as no excess silicate is squeezed from the press.

Wood which has been stained with silicate is difficult to restore by treatment with oxalic acid or bleaching agents on account of the protective film which keeps the reagent away from the stained fibers.

Fiber Board.

The advent of the fiber shipping container made from corrugated or solidly laminated sheets of paper has opened a wide field for silicate adhesives. The heavier laminated paper products such as wall board, cloth board, and paper tubes, have also assumed an important place in industry.[13] Each presents its own problems of adaptation of adhesive to machine and papers. On this account, and because growth is still active, the processes will be separately treated in some detail but always from the point of view of the function of the silicate adhesives. The transition from wood, which is used once and burned, to paper, which can be reclaimed many times is of primary economic significance in a country whose forest reserves are being rapidly depleted in the face of an expanding industrial life and an inadequate program of reforestation.[14]

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[13] Malcolmson, J. D., *Chem. Age,* **28**, No. 8, 273 (1920) ; **28**, No. 9, 321 (1920).
[14] Andrews, O. B., *The Shears,* **34**, 97-105 (1924).

CORRUGATED PAPER.

By this term we understand a structure composed of the actual corrugated sheet with one or two flat sheets to which the tips of the corrugations are adhesively united. Some interesting variations have been proposed.[15-19] The specifications of the Freight Container Bureau and the Bureau of Explosives, which through the railroads and the Interstate Commerce Commission [20] control the classification of containers in the United States, require that the sheet in which the corrugations are impressed shall be made of straw. The great bulk of corrugated paper is used to make boxes for freight transport, so these specifications
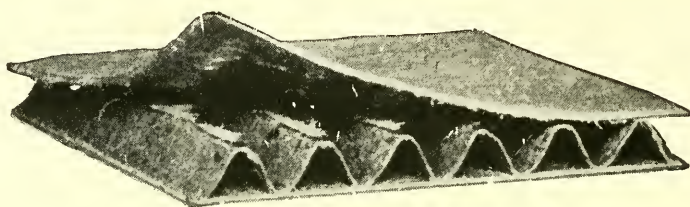
FIG. 101.—Corrugated Paper.

are strictly observed. Although they allow rather wide variations in composition they are of sufficient interest to record.

Specifications.

The thickness of the straw paper for corrugating is 8 to 10 points.* The flat lining sheets are of two types,—a board made of old papers exclusively, called chip board, and a better sheet used on the outer liners. This passes under the misnomer of "jute", though it is usually quite free from this fiber; more properly it is called test board, for it must meet definite strength tests proportioned according to the size and loading of the box. It is generally made from old papers with an addition of sulfite or sulfate pulp and is well-sized with rosin size precipitated on the fiber with alum. A liner of more or less pure sulfate fiber, known as kraft, is coming into increased favor on account of its great strength. The adhesive which combines these three elements, a corrugated sheet between two flat sheets, into a shock-absorbing structure, is silicate of soda. The composition most generally used is

[15] Fiske, William Grant, U. S. Pat. 145,854 (June 29, 1920).
[16] Howard, Charles H., U. S. Pat. 1,605,953 (Nov. 9, 1926).
[17] O'Brien, David J., U. S. Pat. 1,360,142 (Nov. 23, 1920).
[18] Wandel, Kurt, U. S. Pat. 1,519,281 (Dec. 16, 1924).
[19] Fairchild, Walter H., U. S. Pat. 1,158,657 (Nov. 2, 1915).
[20] *Consolidated Freight Classification,* No. 4, 24, Rule 41 (Dec. 20, 1924).
* *i.e.,* 0.008 to 0.010 inch.

TABLE 81. *Fiberboard, Pulpboard or Double-Faced Corrugated Strawboard Containers. Double-Faced Corrugated Strawboard Facings.*

No. of Box	Style of Box	Max. Wt. of Box and Contents (Lbs.)	Max. Outside Dimensions; Length, Width, and Depth Added (Inches)	Solid Fiber Board		Double-faced Corrugated Strawboard, Chestnut or Pine Wood Fiberboard Facings		
				Minimum Thickness of Board	Minimum Cady or Mullen Test (Lbs. per Sq. in.)	Minimum Thickness (Inches)	Minimum Cady or Mullen Test per Sq. In.	Minimum Cady or Mullen Test per Sq. In. of Combined Board (Lbs.)
1	One piece	40	60	0.060	175	0.016	85	175
2	" "	65	65	0.080	200	0.016	100	200
3	" "	90	70	0.100	275	0.030	135	275
4	Telescope	40	60	0.060	175	0.016	85	175
5	"	65	65	0.080	200	0.016	100	200
6	"	90	70	0.100	275	0.030	135	275
7	Recessed end ..	40	60	0.060	175	...	...	...
8	" " ..	65	65	0.080	200	...	...	...
9	" " ..	90	70	0.100	275	...	...	...
10	One piece-	40	60	...	...	0.016	85	175
11	Threefold edge.	65	65	...	...	0.016	100	200
12	Solid body	40	60	0.060	175	...	...	...
13	" "	65	65	0.080	200	...	...	...
14	" "	90	70	0.100	275	...	...	...
15	Double strength corrugated strawboard	90	70	..	...	0.016	85	275

$Na_2O, 3.3SiO_2$ though some variation from this standard has been practiced.

"The best method of closing the bottom of a box by gluing is by means of a press, where it should be allowed to remain undisturbed for at least 3 minutes.[21] The next best method is to glue and immediately fill, allowing the weight of the contents to act as a press for at least 3 minutes undisturbed. The tops may then be glued and the box immediately reversed, thus bringing the weight of the contents on the top, and allowing the box to remain undisturbed for 3 minutes as before; the sealing tapes may be applied to the bottom of the box during this time. The box may then be reversed and the sealing tape applied to the top after which it should remain undisturbed for at least 30 minutes." Complete and adequate closure can be obtained with silicate without the use of tape.

Manufacture. In order to understand the adhesive requirements of this art it is necessary to consider the mechanical conditions imposed by the machines in common use. The straw paper is first moistened

[21] *Consolidated Freight Classification, loc. cit.*, p. 23.

by a jet of steam and then ironed into permanent waves by passing steam-heated bronze corrugating rolls. In the best practice, silicate is applied to the tips of the corrugations while they are engaged in the teeth of a metal roll and the first backing sheet is laid on them under substantial pressure limited only by the danger of weakening or defacing the flat sheet. Under these conditions of heat corresponding to three or more atmospheres of steam, and solid contact, the adhesive may be applied very sparingly and will set almost instantly to a condition stronger than the paper. To secure this result the sheets must be pressed together very soon after the adhesive is spread; the machines shown in the diagrams will do it in a fraction of a second.

Thus a single-faced paper with thirty-six corrugations to the foot may be made with 0.0488 kilo of 40° silicate per square meter (ten pounds of 40° silicate per 1000 square feet).

The case is quite different with the second sheet. The evolution of
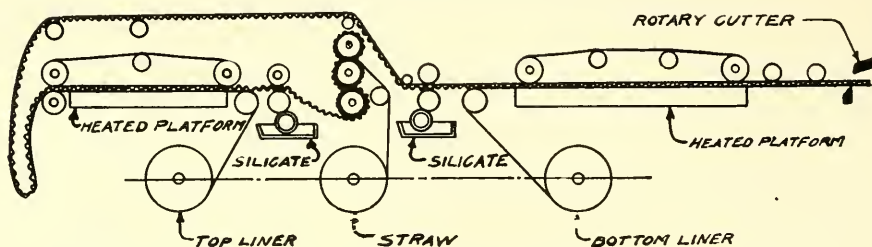
FIG. 102.—Machine for Making Double Faced Corrugated Paper.

machinery for this purpose has provided means for applying the second lining sheet quickly after the silicate is spread. This avoids the need for excessive amounts which serve only to delay the set long enough to permit wetting and making a good contact with the second liner, but it is obvious that no greater pressure can be applied than that which the paper truss will carry. For this reason more silicate is required to put on the second sheet. It is good practice to use 0.0586 to 0.0732 kilo per square meter (twelve to fifteen pounds per 1000 square feet), but this varies with mechanical conditions.

When the silicate is applied from below it tends to run into instead of away from the point of contact, which makes for economy. These machines are run at speeds up to more than a hundred linear feet a minute. The first liner sticks without any treatment; the second is set by passing over a steam-heated table with a device for maintaining contact. Some machines provide insufficient steam table to effect complete setting, which occurs only after the sheets have been stacked in

piles. Fans are sometimes provided to remove the steam by blowing down the length of the corrugations.

To make boxes, the finished paper must be scored and as the bend
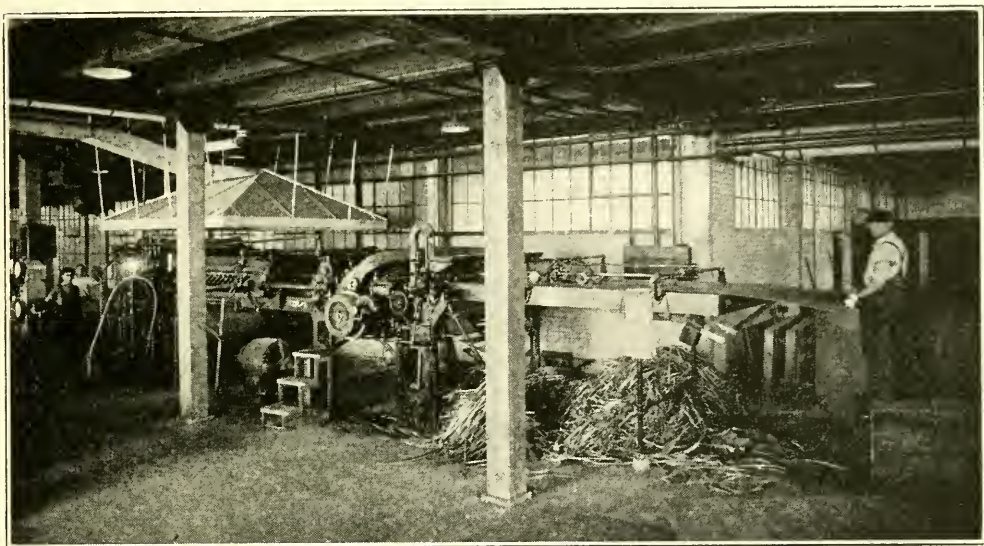
Fig. 103.—Making Corrugated Paper.

is a source of weakness a strip of reinforcing paper is sometimes silicated to the lining sheet as it moves along.[22]

The history of the various manufacturing processes can be followed by a study of the patents given below.[23-46]

[22] Bird, Charles S., U. S. Pat. 1,022,923 (April 9, 1912).
[23] Jones, A. L., U. S. Pat. 122,023 (Dec. 19, 1871).
[24] Melch, H. B., U. S. Pat. 212,723 (Feb. 25, 1879).
[25] Thompson, R. H., U. S. Pat. 252,547 (Jan. 17, 1882).
[26] Thompson, R. H., U. S. Pat. 430,447 (June 17, 1890).
[27] Ferres, J. T., U. S. Pat. 545,354 (Aug. 27, 1895).
[28] Ferres, J. T., U. S. Pat. 657,100 (1900).
[29] Hinde, U. S. Pat. 1,005,836 (1911).
[30] Raffel, T. E., U. S. Pat. 1,146,771 (July 13, 1915).
[31] Hicks, O. H., U. S. Pat. 1,184,748 (May 30, 1916).
[32] Langston, S. M., U. S. Pat. 1,186,997 (June 13, 1916).
[33] Langston, S. M., U. S. Pat. 1,186,998 (June 13, 1916).
[34] Swift, George, U. S. Pat. 1,263,000 (April 16, 1918).
[35] Swift, George, U. S. Pat. 1,410,622 (March 28, 1922).
[36] Swift, George, U. S. Pat. 1,425,914 (Aug. 15, 1922).
[37] Hill, Irving, and Paul A. Dinsmoor, U. S. Pat. 1,473,096 (Nov. 6, 1923).
[38] Spaeder, L. J., U. S. Pat. 1,535,503 (April 28, 1924).
[39] Heinrichs, Berg, U. S. Pat. 1,482,894 (Feb. 5, 1924).
[40] Swift, George W., U. S. Pat. 1,492,490 (April 29, 1924).
[41] Maston, Edward E., U. S. Pat. 1,493,763 (May 13, 1924).
[42] Colgrove, Charles E., U. S. Pat. 1,569,073 (Jan. 12, 1926).
[43] Howard, Charles H., U. S. Pat. 1,605,953 (Nov. 9, 1926).
[44] Wagner, Joshua, U. S. Pat. 1,620,174 (March 8, 1927).
[45] Kramer, Joseph, and Albert H. Israel, U. S. Pat. 1,629,511 (May 24, 1927).
[46] Crowell, Charles H., U. S. Pat. 1,631,521 (June 7, 1927).

Effect of Age. Malcolmson [47] has investigated the condition of corrugated container board after it had been stuck together with silicate for ten years and found it still of satisfactory quality. The strength

STRAW STEAM E F COCOA MATS H J K G HEATING PLATENS 8'-0" TO 16'-0" A B C D HEATED DRUM.
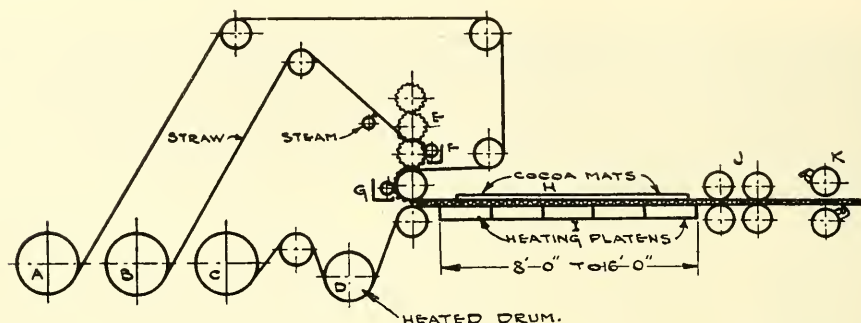
FIG. 104.—Double Faced Corrugated Paper. Silicate Applied at F and G.

TRAVELING GUILLOTINE CUTTER
RUBBER COVERED PULL ROLLS
HEATED PLATFORM
SILICATE
BRUSHES
TOP LINER BOTTOM LINER STRAW
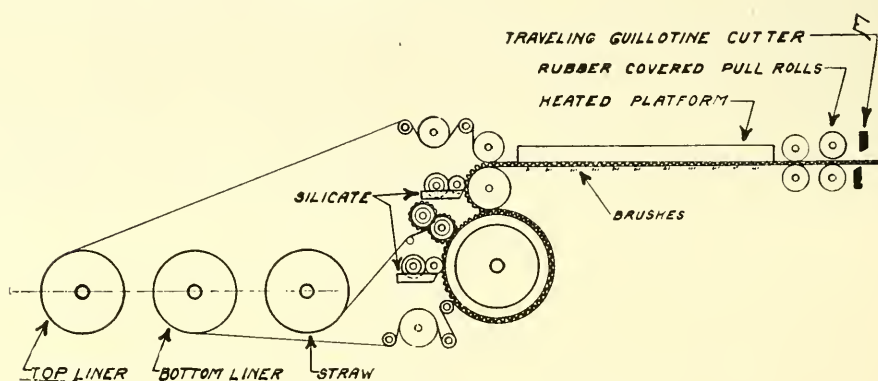
FIG. 105.—Double Facing Corrugator.

SINGLE FACER DOUBLE FACER CUTTER
SILICATE HEATED PLATFORM
SILICATE
SILICATE
TOP LINER STRAW BOTTOM LINER
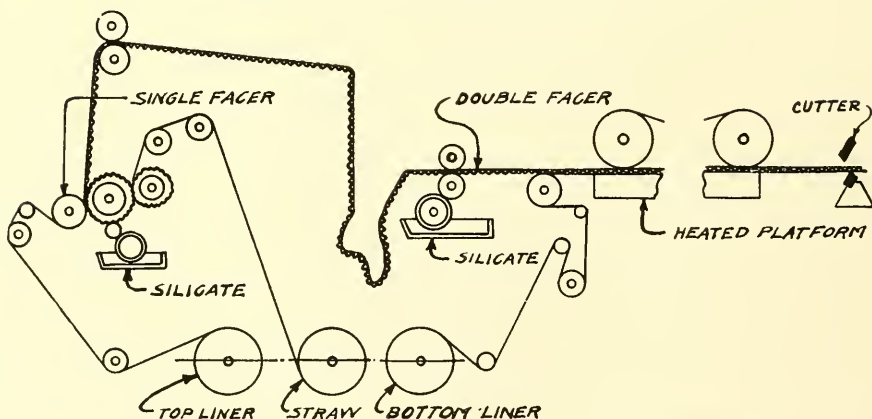
FIG. 106.—Single and Double Facer as Separate Units.

of the paper is such that no great adhesive strength is needed, so that the initial strength of the silicate can be much reduced by carbonating without depreciating this product.

[47] Malcolmson, J. D., *Fibre Containers,* 6, No. 3, 10-11 (1921).
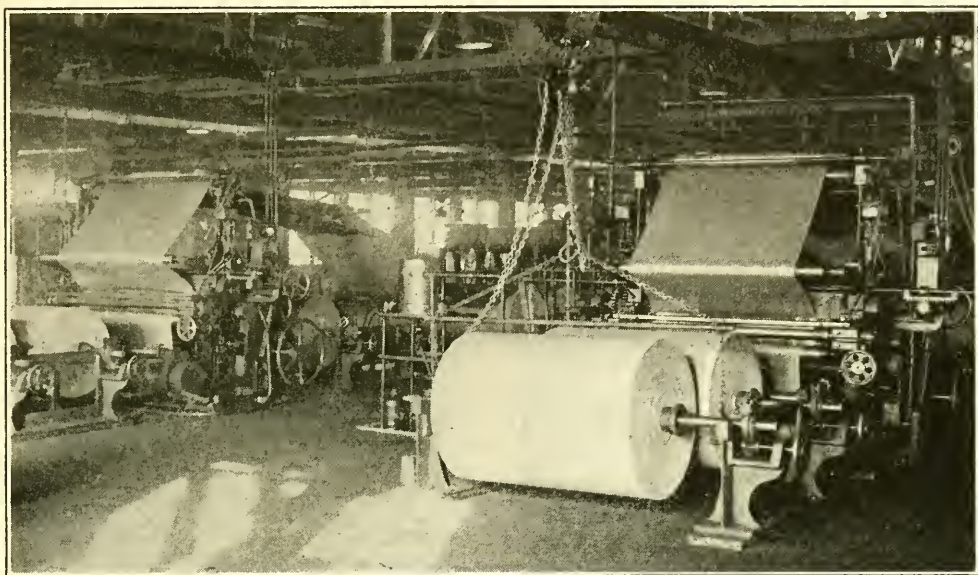
Fig. 107.—Making Corrugated Paper.
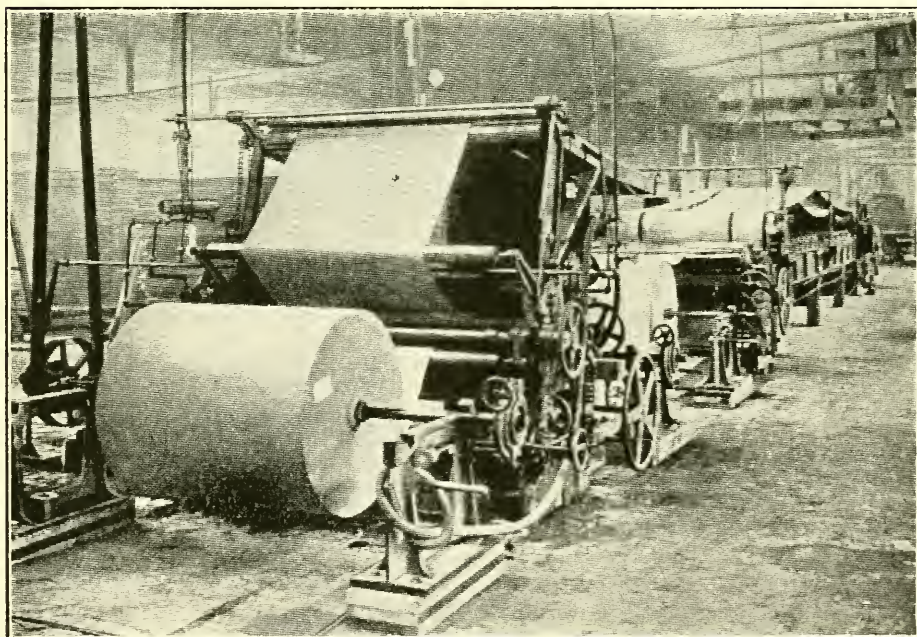
Fig. 108.—Corrugator, Single and Double Facer in Tandem.

Effect of Moisture. One of the fundamental economies of the paper shipping container is the feasibility of putting it into the beater of a paper mill and making it into fresh paper after it has done its initial service.   This means that it must be possible to reduce it to pulp with water.   Not only old containers but the trim and waste from the combining machines must be reworked.   With this, an absolutely water-proof adhesive is incompatible.

Silicate without any additions to increase its water-resistance not only makes a board that can be reworked, but if precipitated with alum
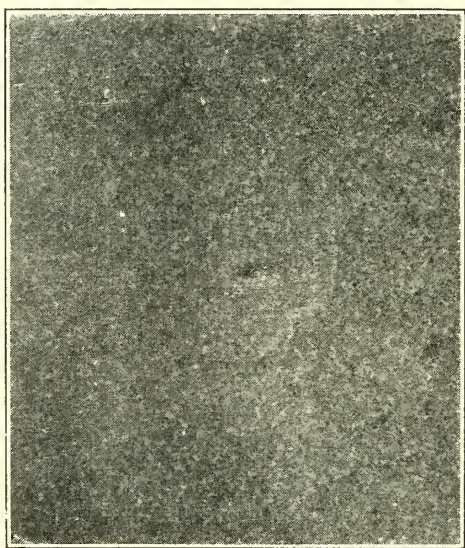
FIG. 109.—Board Made with Silicate Containing 9% Na₂O as Applied. Water Applied by Inverted Glass for 7 Hours.
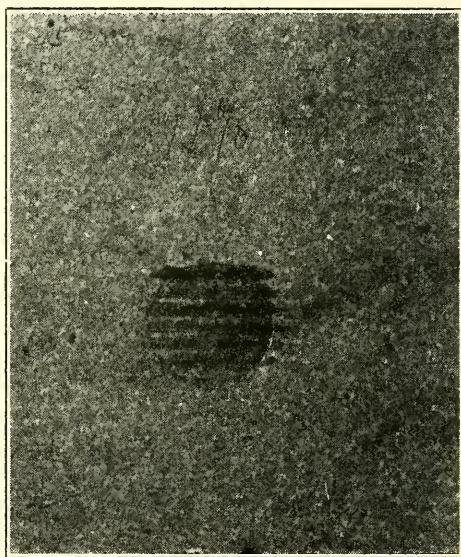
FIG. 110.—Board Treated Identically with Fig. 109, Differing from It Only in That the Silicate with Which the Board Was Made Contained 11% Na₂O.

it imparts a hardening effect to the new sheet and improves its surface and strength.   Silicates are added for this purpose to many paper stocks in which they do not occur accidentally, or better incidentally, as adhesives.

Water-Resistance.   Rosin size is depended on for water-resistance in container board; it is adversely affected by alkalies, and all adhesive silicates are alkaline.   The remedy lies in using silicates of the lowest alkalinity consistent with mechanical necessity, in applying them as sparingly as may be to give good adhesion, and in causing them to dry in the shortest possible time, thus localizing their effect.

Water tests were made by inverting a drinking glass full of water on sheets made from the same paper but different silicates (Figs. 109 to 112).

The photographs show the penetration of water after seven and fifteen hours with $Na_2O, 3.3SiO_2$ and $Na_2O, 2.9SiO_2$. Translated into the conditions of a box in a rainstorm, the difference, which corresponds to but 2 per cent Na_2O, is the difference between success and failure. The more alkaline silicate is attractive on account of its greater tackiness, but for the reason given it should never be used within one thickness of paper from the outside of the box.

This consideration does not apply to the adhesive used for sealing these containers, for the sealing silicate is always at least three layers of paper away from the outside and does not penetrate to the surface.
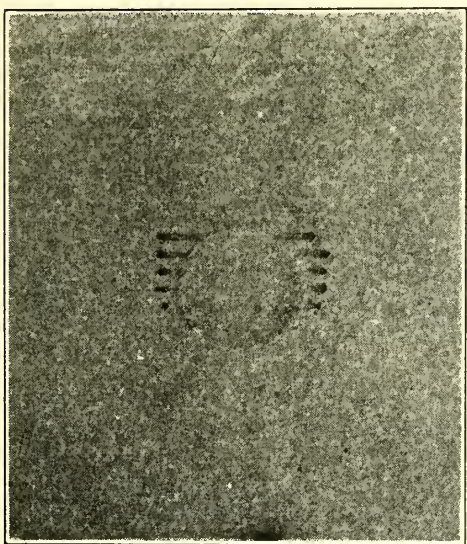
Fig. 111A.—Board Made with Silicate Containing 9% Na_2O as Applied. Water Applied by Inverted Glass for 15 Hours.
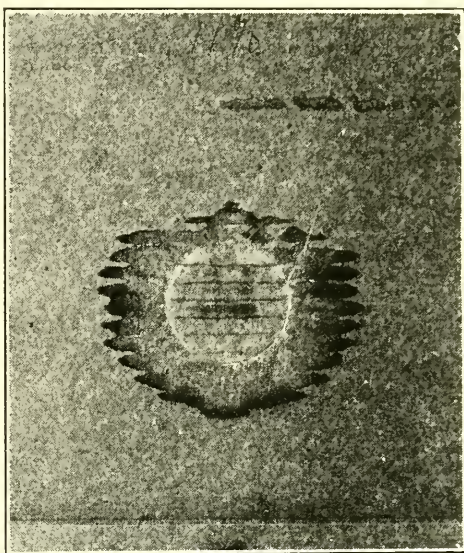
Fig. 111B.—Board Treated Identically with Left Hand Specimen, Differing from It Only in That the Silicate with Which the Board Was Made contained 11% Na_2O.

Alkalinity. The lowest practical alkalinity for adhesive use is near $Na_2O,4SiO_2$.[48] The water test was applied to some board made with this silicate. When stored dry the rosin size was not affected. Storage of a month over water in a closed vessel, followed by the water test, gave a sharp contrast between $Na_2O, 3.3SiO_2$ and $Na_2O,4SiO_2$. Figure 112 is the obverse view.

Sealing. Corrugated shipping cases are sealed with silicate adhesive spread by hand or mechanically. As in the manufacture of the board, the most economical results are obtained where a firm pressure is applied as soon as the silicate is spread. This is easily provided in

[48] Stericker, Wm., U. S. Pat. 1,462,835 (July 24, 1923).
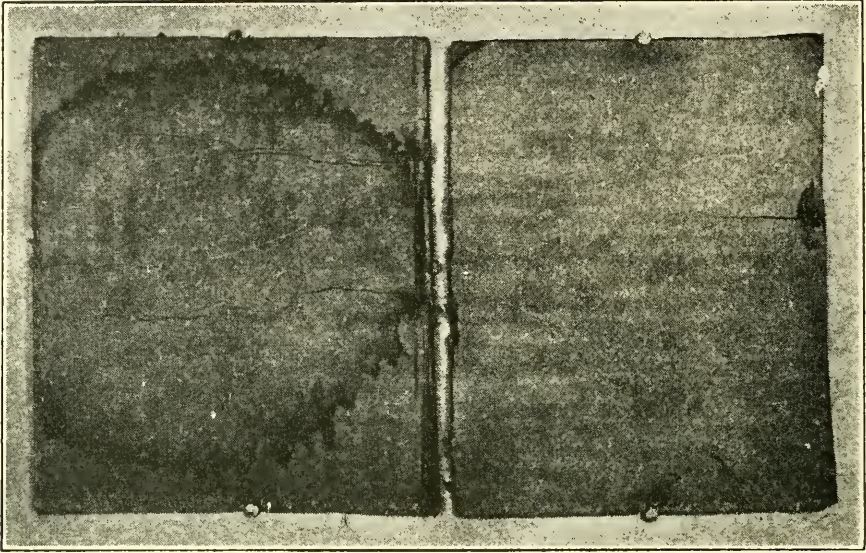
FIG. 112.—Corrugated Paper. Comparison of Water Resistance with Silicate, Ratio 1 : 3.3 and Ratio 1 : 4.
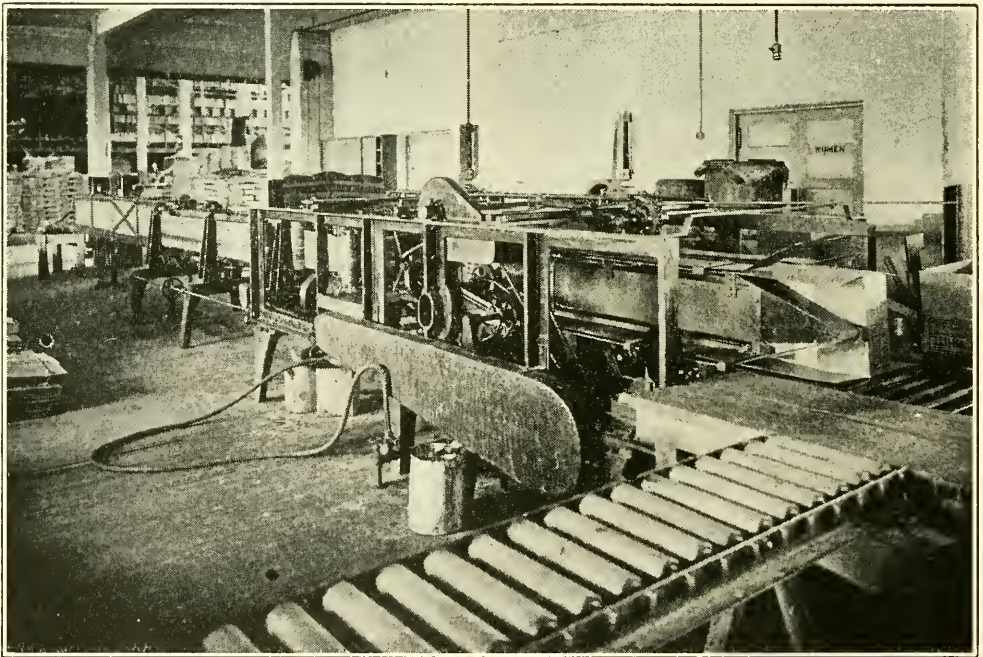
FIG. 113.—Automatic Silicate Sealing of Fiber Containers.

setting up the box and sealing the bottom before filling but much more difficult after the container is packed with some light or fragile ware.[49]
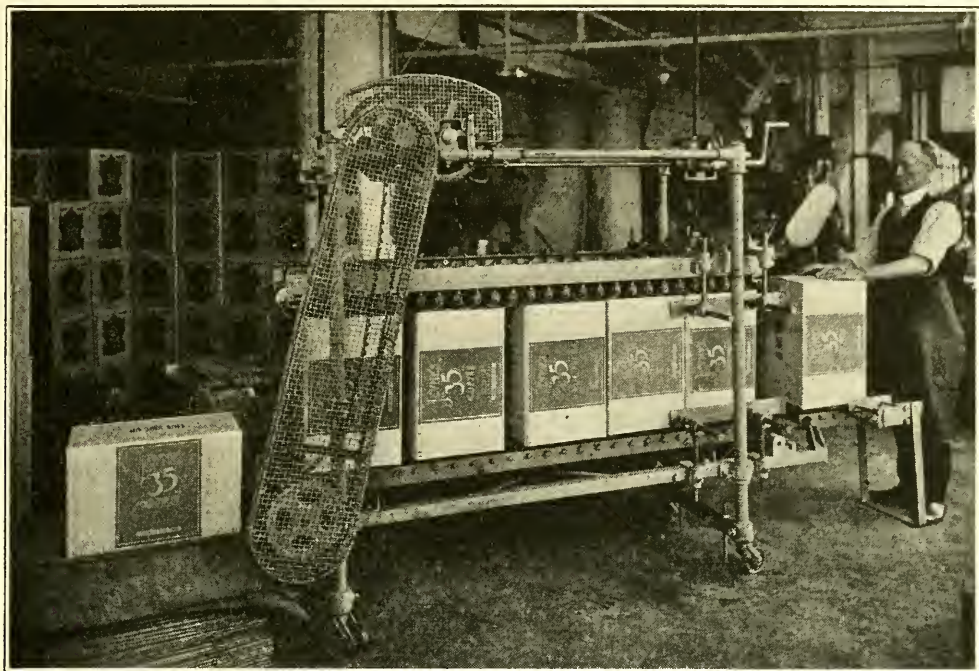
Fig. 114.—Silicate Sealing Fiber Containers. Silicate Spread Manually.

The greatest measure of success is believed to be obtainable with a silicate close to the composition $Na_2O, 2.9SiO_3$ concentrated to a vis-
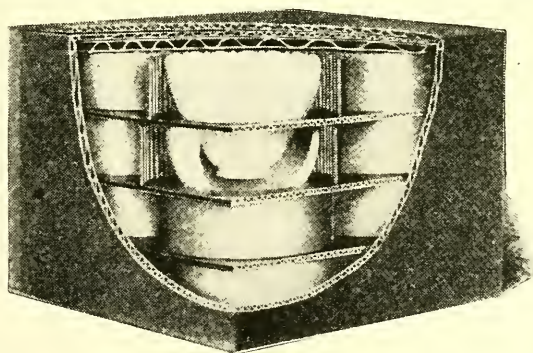
Fig. 115.—Glassware in Corrugated Paper Box.

cosity of 800 centipoises which corresponds to a specific gravity near 1.48

This solution weighs 1.47 kilograms per liter (12.3 pounds per U. S. gallon) and this amount will seal 300 boxes 30.5×30.5 centimeters

[49] "Packing for Domestic Shipment," U. S. Dept. of Commerce, Domestic Commerce Series No. 10, p. 10, **1927.**

(12 × 12 inches), with careful hand spreading using a brush, or 27.87 square meters (300 square feet) of flap area. On boxes which have been highly sized it is needful to dilute the silicate to obtain the best grip on the paper. This process increases the spread but necessitates special precaution to obtain good contact. Ten per cent of added water will give a spread of about 9.45 square meters per liter (385 square feet per gallon) while 25 per cent increases this to approximately 14.7 square meters per liter (600 square feet per gallon).

The Forest Products Laboratory [50] determined, by a series of tests, that maximum strength of the silicated joints of fiber boxes was not reached until 4 hours had been given the silicate of soda for setting. The tendency of the board to absorb water from the silicate causes a weakening of the silicate joint between the jute and the chip. Before the board can reach its maximum strength, this water must have been evaporated through it, which because of its thickness is a slow process. Their tests showed that temperature had an effect on the rate of drying of the silicate joint only under extreme conditions; at normal working temperatures no effect could be detected.

Silicate adhesives when they have set in the air as on brushes or machine parts are more difficult to remove than glue or dextrin. It is therefore wise to keep all machinery in contact with silicate thoroughly clean. This is easily accomplished by treatment with hot water or a steam jet at the close of each working period. Failure to attend to this may involve a laborious operation of chiseling away the accumulation or the less satisfactory expedient of dissolving it off with a hot caustic soda solution. The other side of the balance is that the silicate adhesives are sterile, odorless, and inexpensive. They are supplied at controlled viscosities ready to use and thus repay the care required to use them.

Laminated Board

Specifications. While corrugated board is best adapted for fragile goods, there is great demand for a paper container of maximum strength which need have no shock-absorbing properties. To meet this, chip board is laminated flat with a silicate adhesive. It is not economical to make thick paper upon the ordinary paper machines.[51] Thirty points, that is, thirty thousandths of an inch, is the maximum for container stocks on account of the slowness of drying. If there

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[50] Hale, H. M., Second Progress Report, Project L-207-4, Forest Products Laboratory, Madison, Wis.: March 11, 1919.

[51] Malcomson, *loc. cit.*

are exceptions for special purposes this is certainly true of chip board and container test board, the production of which engages the largest paper machines thus far built. They must operate at high speed and minimum cost. Sixteen points is the thickness of most of these products. One machine with which the author is familiar makes a sheet 154 inches wide, 16 or 20 points thick, and runs at 250 feet per minute, producing 178 tons of paper daily.

In order to make boxboard it is usual to combine chip board inner sheets with liners of higher test and water-resistance. The liner when folded into a tray must hold water for 6 hours and must meet the specifications given below:

TABLE 82. *Specifications for Solid (Laminated) Box Board.*

Minimum Thickness of Board (In.)	Required Strength, Mullen Test (Lbs.)	Maximum Combined Dimensions, Length and Width and Depth (In.)	Maximum Gross Weight Package and Contents (Lbs.)
0.060	225	60	40
0.080	275	65	65
0.100	325	70	90

The silicate, according to these specifications, should conform to the following analysis:

"(a) For manufacturing plyboard the ratio of soda to silica must not be greater than 1 to 2.8 with a specific gravity not exceeding 47°Baumé at 68°F., and it is recommended that silicate of soda having ratio of soda to silica not exceeding 1 to 3.25 with a specific gravity not exceeding 43°Baumé at 68°F. be used where manufacturing conditions permit.

"(b) The silicate of soda must be as evenly spread as possible and should not exceed in amount from 15 to 18 pounds per 1,000 square feet of each film of cement used in the board.

"(c) For cementing the closures of plyboard boxes the ratio of soda to silica must not be greater than 1 to 2.8 with a specific gravity not exceeding 47°Baumé at 68°F., nor be less than 1 to 3.0 with a specific gravity not less than 41°Baumé at 68°F."

Manufacture. Meeting of the specifications is accomplished by building up a combined board three-, four-, or five-ply. The silicate used is ordinarily $Na_2O, 3.3SiO_2$, but it may be less viscous than that used for corrugated board. The usual method of application is to draw the inner sheets through a silicate bath and then to bring them together with the dry liner sheets between heavy press rolls which squeeze out any excess silicate and allow it to drain back into the main supply. A series of other press rolls keeps the paper in contact as it passes to the cutting end of the machine. The operation is conducted without heat and very rapidly. Two hundred linear feet per minute is usual. As the machine may be less than fifty feet from the first press roll to the cut off where the board must be ready to make

into boxes it will be seen that the silicate must set in less than fifteen seconds. This is possible by the use of very thin films and great pressure. Obviously all the water lost to set the silicate must be absorbed into the paper, as there is no opportunity for evaporation. If the paper contains before combining the amount of water which gives optimum strength, the combined board will be weaker than the sum of its plies, but if it be drier at first the silicate may add water which gives the appearance of increased strength. As the board comes into equilibrium
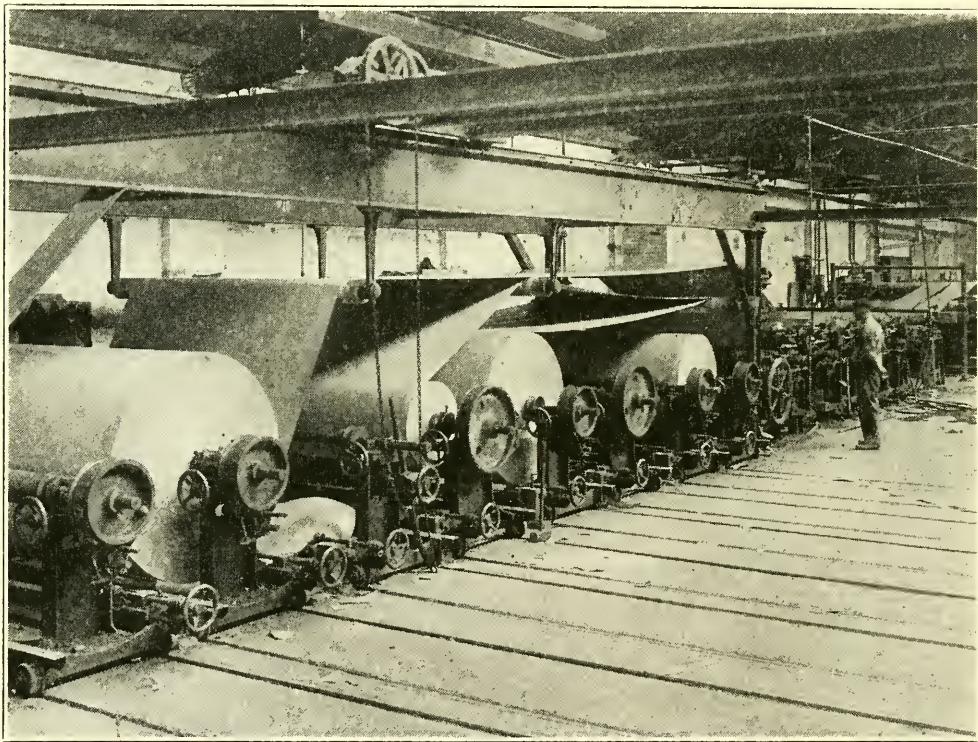
Fig. 116.—Laminating Fiber Board with Silicate of Soda.

with the air its normal strength will appear and it is this which should govern the selection of materials to meet a given test.[52]

Under modern practice the silicate films are so thin as easily to escape detection. A convenient way to observe them is to cut the board diagonally with a sharp knife, moisten the edge, and apply a drop of phenolphthalein solution, when the pink color will locate the silicate line and show that there is very little penetration into the board.

A normal spread of silicate for a smooth chip and jute combination is near 0.17 kilo of 1.38 specific gravity (40° Baumé) solution per

[52] Kress, Otto, and Philip Silverstein, "How Paper is Affected by Humidity," L-10, 529 (1917), Forest Products Laboratory, Madison, Wis.; presented at Annual Meeting Tech. Ass. of Pulp & Paper Industry, New York (Feb. 8, 1917).

square meter (35 pounds of 1.38 specific gravity solution per 1000 square feet) of three-ply board. Slightly better spreads can be had by using $Na_2O, 3.9SiO_2$ on account of its still smaller tendency to penetrate the paper.

Maximum water-resistance is sometimes secured in a board of this type by introducing as one of the interior plies a sheet containing a film of asphaltic material.[53]

Sealing. Solid fiber boxes are sealed in much the same way as corrugated, but it is to be noted that when there are asphaltic layers so near the surface that the board will not take up enough water to set the silicate in a short time, the bond forms very slowly.

The design of paper shipping containers has been carefully worked
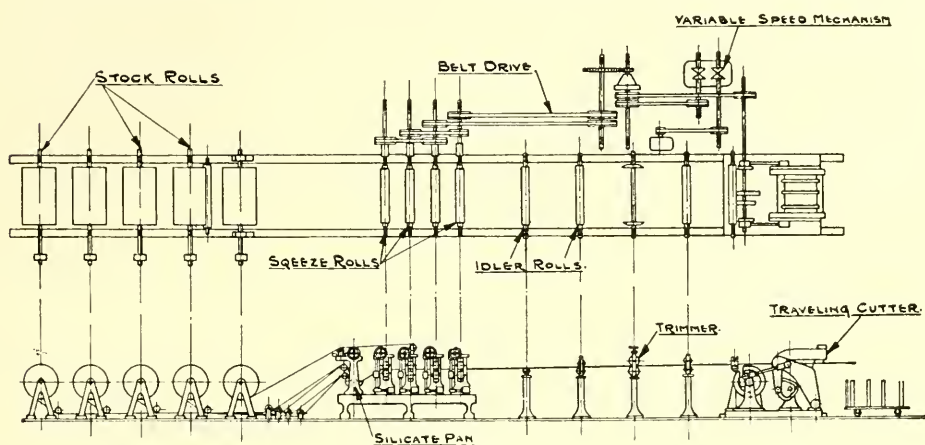
Fig. 117.—Plan and Elevation of Combiner for Solid Container Board or Wall Board.

out and points of weakness determined by the aid of a rotary drum tester which simulates the hazards to which boxes are subject in traffic. The silicate bond is always stronger than the substance of the paper. The silicate seal for closure stiffens the box by uniting the whole contact surface of the flaps at top and bottom and when properly made never fails.

Wall Board. Thick combined boards for book-backs, cores for wrapping bolts of cloth, lithograph supports for advertising display, et cetera, are often laminated in sheet form instead of continuously from rolls. Thus any desired thickness can be built up and put into a press to set in a few minutes. The time required to build up a pile is long enough to make necessary a more liberal spread. Wall board [54]

[53] Davidson, Frank B., U. S. Pat. 1,353,323 (Sept. 21, 1920).
[54] Sandor, Nikolaus, Ger. Pat. 389,536 (1924); *Papier-fabr.*, **22**, pt. 84 (Mar. 2, 1924).

Fig. 118.—Drum Tester. (By courtesy of Container Testing Laboratories, Inc., Rockaway, N. J.)
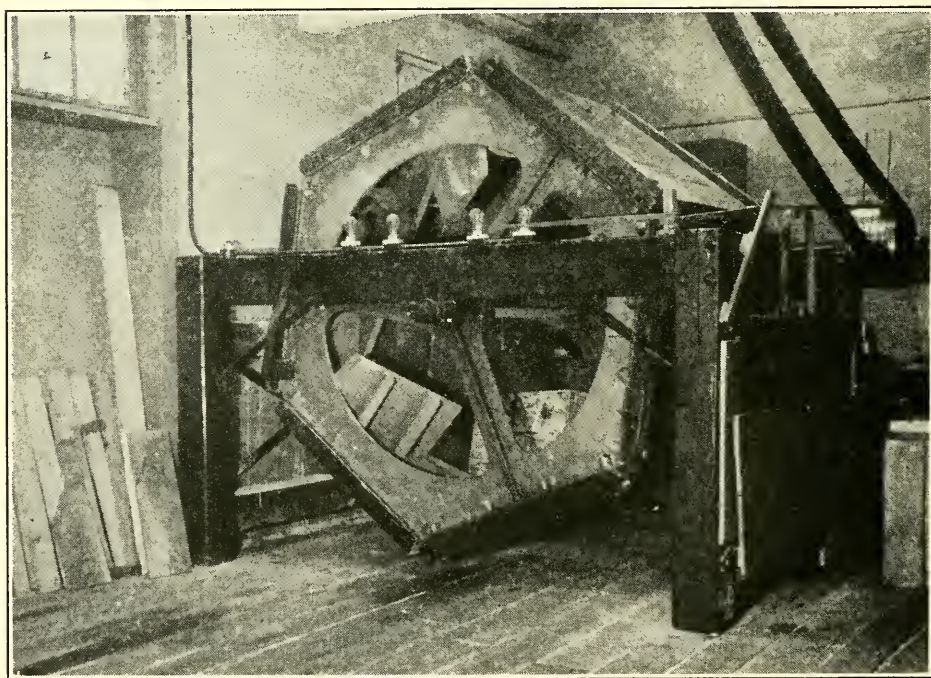
Fig. 119.—Drum Tester. (By courtesy of Container Testing Laboratories, Inc., Rockaway, N. J.)

for interior building construction is laminated continuously but differs from container board in that the plies are usually thicker, about 0.127 centimeter (0.050 inch), and finished with a rougher surface. Built up four-ply they require a thicker silicate and a heavier spread, for the finished product must be as stiff as possible; 0.248 kilo per square meter (50 pounds per 1000 square feet) of four-ply board is usual. This industry has in recent years reached substantial proportions.

A piece of wall board shown in the cut was built into a house in the tropics where it was attacked by white ants. They cut an intricate series of passages as shown, but ate the wood pulp down to the first silicate layer only. It is not known whether the taste of the silicate or the hardness of the film was the determining factor, but more likely the latter as silicate of adhesive grades tastes to us not unlike baking soda
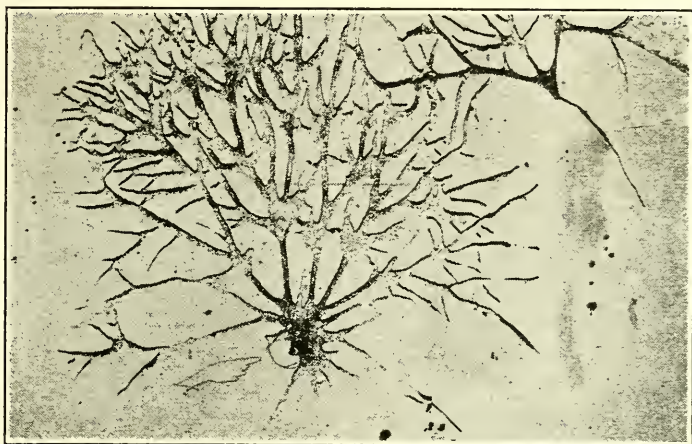
Fig. 120.—Wall Board Attacked by White Ants.

and very much milder than the same amount of Na_2O, as hydroxide. The tendency of silicate films to repel vermin is a distinct advantage when it is used for containers for the transport of food or other commodities likely to be attacked.

MISCELLANEOUS USES.

Paper Tubes. Paper tubes present a set of adhesive requirements quite different from either corrugated or flat laminated papers.* Spirally wound tubes are made from narrow strips of paper drawn around a mandrel by the friction of leather belts. Except for large diameter tubes or tubes made on machines which move slowly enough for the silicate film to become sticky after spreading, the chief difficulty lies in a tendency of the paper to slip and fold under the traction of

* Cf. page 244.

the belt. Mechanical improvements are tending to minimize this disadvantage and some small tubes are made with silicate adhesive. $Na_2O, 3.3SiO_2$ is used to make the 12-inch diameter tubes shown in the illustration and some smaller tubes are made with more alkaline types up to $Na_2O,2SiO_2$, but this use has not developed to the extent that would be possible with a power-driven spreading device. $Na_2O,2SiO_2$ has just the needed properties of stickiness and quick set at 61°Baumé, but its viscosity is too great to permit handling it satisfactorily on machines built for the much more fluid hot animal glue solutions which become sticky by cooling immediately after spreading.

A conically wound paper barrel shown in Figure 123 is another
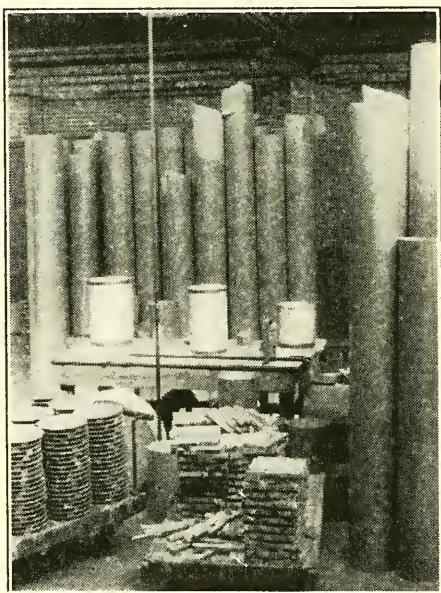
FIG. 121.—Spiral Wound Containers.
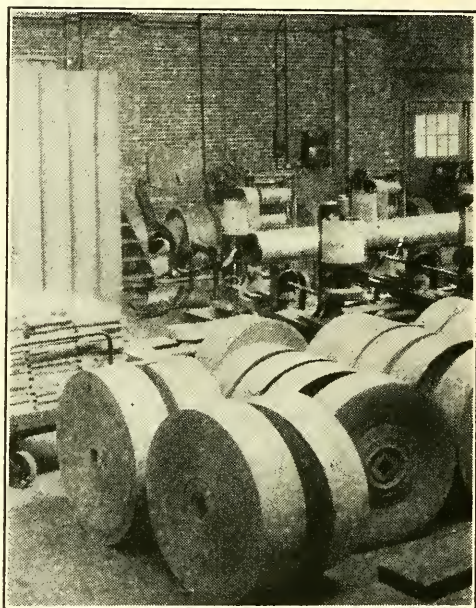
FIG. 122.—Straight Sided Paper Barrel Making with Silicate Adhesive.

variation of the use of silicate adhesives on paper.[55] Convolute or straight wound tubes are also easily made with silicate solutions as adhesives.

Label Pasting. Label pasting with silicates is widely practiced where labels printed in black are used, as on rolls of paper. Silicate solutions give good adherence on clean tin plate, but on thin papers it is necessary to avoid colors which are sensitive to alkali. Papers which contain large amounts of mechanical wood pulp or unbleached fibers are likely to show some discoloration when thin sheets are pasted with it. This is reduced to a minimum by using $Na_2O,4SiO_2$, spreading it very thin, and drying quickly to prevent penetration.[56]

[55] Snyder, George C., U. S. Pat. 1,270,889, 1,270,890, 1,270,891 (July 2, 1918).
[56] Furness, Rex, *J. Soc. Chem. Ind.*, **41**, 18, 381 R-384 R (1922).

Splicing Felt Paper. Silicate solutions have been found the most satisfactory adhesives for splicing felt paper which is to be drawn through a bath of hot asphalt for saturating to make roofing because it sets quickly and resists for a sufficient time the temperature of the bath.

Silicating Watch Screws. A certain watch manufactory places minute screws in position for polishing by drawing them with a partial vacuum into holes in a polishing head. When the screws are in place the head is painted with a viscous silicate which holds them in
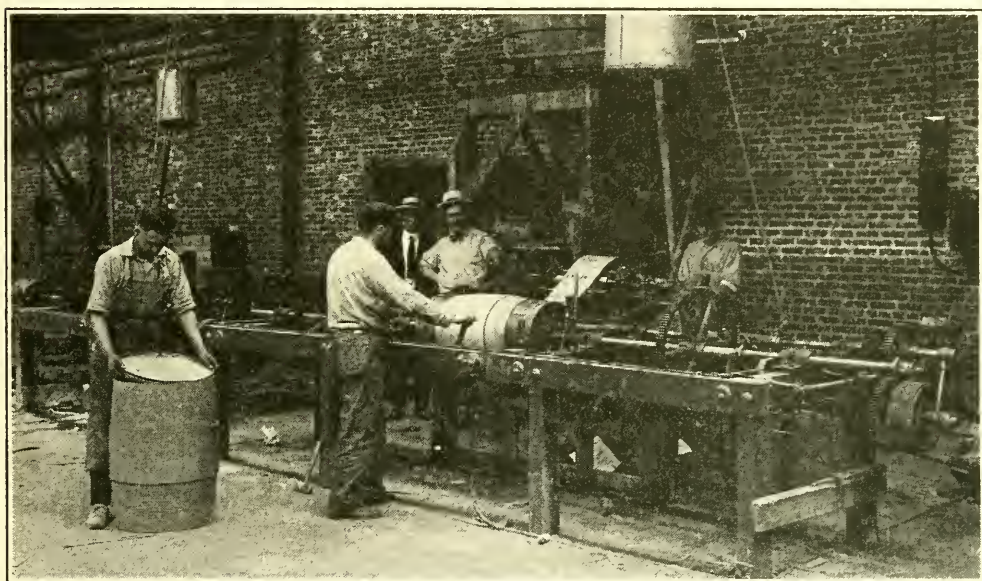
FIG. 123.—Tapered Paper Barrel Made with Silicate Adhesive.

place. The vacuum is then released and the heads are polished with minimum labor.

Instances of adhesive uses of pure silicates could be multiplied but those described will give an idea of the behavior of the adhesive solutions by themselves, and we shall next consider adhesive mixtures.

Adhesive Mixtures.

Mixtures with Insoluble Inorganic Powders.

Wall Board Requirements. Wall board being much heavier than container board and having three thick adhesive layers to help stiffen it, is passed more slowly through the combiner than stock with very thin silicate films. The viscosity of the films increases more gradually, the adhesive is slow to set. Also because the board is heavy and

more difficult to handle, the machines are stopped relatively often for adjustments, and rolls of paper of 0.050 inch thickness contain less area than like weights of thinner stock. On these accounts it is desirable to use an adhesive which will remain sticky on the part of the paper which has been spread and not pressed together. Here surface evaporation comes into play and $Na_2O, 3.3SiO_2$ will lose its ability to wet the dry liner sheet within about two minutes. A natural remedy would be to use a more alkaline silicate which remains sticky for a longer time. $Na_2O, 2.9SiO_2$ has been used and with it a waiting period of about seven minutes is possible. Its behavior on the machine is satisfactory—it holds the edges well and gives a minimum loss from imperfect sheets.

Diffusion of Sodium Compounds. The relative water-resistance of these two types of silicate was illustrated in describing corrugated paper. The wall board being made cold and having three thick layers of silicate between heavier paper cannot dry as quickly as container board, and this favors diffusion of sodium compounds through the board and liability to stain. The mechanism of this transfer has not been entirely explained, but it is not a simple case of diffusion of silicate. There is a sort of dialysis at work which leaves most of the silica where it was first laid and the sodium-bearing solution which penetrates contains relatively little silica. Similar phenomena occur with other alkaline colloids used as adhesives. The remedy is to use the lowest practicable ratio of Na_2O in the silicate and to dry the films as quickly as possible.

Addition of Hydrous Clay. In the case of wall board, however, this does not provide for the slow setting requirement. Carter [57] solved the difficulty by diluting the less alkaline silicate and thus controlling the rate of set and then restoring the viscosity by adding a powdered hydrous clay.

The rate of set could thus be controlled to a nicety. $Na_2O, 3.3SiO_2$ could be used as dilute as 1.31 specific gravity (35° Baumé). The watery liquid made up with clay to the consistency of thick cream yielded an adhesive abundantly strong which spread at almost the same rate per unit of volume as the pure silicate, but because the mixture contained 45.3 kilos (100 pounds) of silicate solution and 36.2 kilos (80 pounds) of clay the units of sodium oxide per unit of area were reduced and likewise the water per unit area. The process has been in satisfactory use for several years.[58]

[57] Carter, John D., U. S. Pat. 1,188,040 (June 20, 1916).
[58] Thickens, J. H., U. S. Pat. 1,377,739 (May 10, 1921).

Specific data on such a use are apt to be misleading because the varying conditions of different clays have very different effects on the viscosity of the adhesives. These variations are probably a function of particle size but have not been fully studied. The viscosity of silicate-clay mixtures rises for some time after the ingredients seem to be well mixed. This may be due to the wetting of particles which cannot be seen because they are covered by liquid masses. These mixtures can be stored in tanks and pumped with centrifugal pumps.[59]

Other fillers have been tried but their flowing characteristics are less satisfactory,—they spread poorly, or, as the operators say, they work "short" and have more tendency to settle out. This may also be merely a matter of particle size. McBain[60] concluded that finely divided silica had no effect on the strength of a silicate bond.[61]

Addition of Calcium Carbonate. Adhesives made from calcium carbonate and $Na_2O, 3.3SiO_2$ have been employed for the type of wall board which comprises a row of wooden lath laid edge to edge and lined on both sides by paper.[62, 63] Here again, adjustment of fineness and concentration of the silicate are the means of adapting the adhesive to mechanical necessities. By using $Na_2O,2SiO_2$ a greater resistance to water could be secured though the actual silicate used is more soluble.

Although straight silicate solutions give good bonds on plywood made from gum and poplar, the results are less satisfactory on those cut from harder woods, such as maple and birch. It has been found that good adhesion can be had on these woods by adding to a 1.38 specific gravity (40°Baumé) solution of $Na_2O, 3.3SiO_2$ about 30 per cent of its weight of finely divided calcium carbonate. Such a mixture can be spread at the rate of 0.236 kilo per square meter (178 pounds per 1000 square feet) of double glue line and is satisfactory for plywood for shipping cases. Other fillers have been tried without success on these woods, but the reason for the special virtue of calcium carbonate is not known.

A mixture of 25 parts 1.71 specific gravity (60°Baumé) solution of $Na_2O,2SiO_2$, 25 of water, and 60 whiting, when spread upon paper boards becomes substantially insoluble in a week, and the board when redried is found to be stuck together, but while wet the bond is weak. It is strong enough to hold paper but insufficient for plywood.

[59] Thickens, *loc. cit.*, and U. S. Patent Serial No. 3,396, Interference No. 41, 800 (1919).
[60] "Second Report of Adhesives Research Committee," London: His Majesty's Stationery Office, **1922**, p. 81.
[61] Schleicher, U. S. Pat. 1,162,712 (Nov. 30, 1915).
[62] Magelssen, N., U. S. Pat. 1,487,255 (March 18, 1924).
[63] Smith, R. H., and R. B. Beal, U. S. Pat. 1,513,191 (Oct. 28, 1924).

Silicate-Carbohydrate Mixtures.

Starches. Starches boiled in silicate solutions may yield adhesives strong enough to be used on wood veneer, that is, having a tensile strength up to 35.2 kilos per square centimeter (500 pounds per square inch) between maple blocks glued end to end, but they carry much more water than the silicate solutions and for most purposes have little advantage over them. Some care must be given to proportion the mixtures so that they remain homogeneous. Two formulas which have been tested are given.

TABLE 83. *Formulas for Silicate-Starch Mixes.*

1.

100 parts by wt. $Na_2O, 3.34SiO_2$ 1.37 specific gravity.
  5 parts of starch, mixed with 4 parts water, and stirred with the silicate.
Heated until starch loses milky whiteness, becoming nearly clear.

2.

50 parts starch ⎫
100 parts water ⎭ Stirred together.
Heated with 50 parts $Na_2O, 3.34SiO_2$ 1.38 specific gravity until mixture is nearly clear.

The question as to whether the presence of starch would delay the decomposition of silicate adhesives by carbon dioxide was investigated with a negative result.

Dextrin. Silicates may be added to dextrin adhesives for making spirally wound paper tubes and other uses where a low tensile strength suffices and a high degree of initial "tack" is required.* The adhesive film is somewhat more flexible than film that would be formed by the silicate alone, but less than the straight dextrin. The stiffening is often an advantage.

Silicate-Casein Mixtures.

Waterproof Glue. It has long been known that useful adhesives can be made from casein, lime, and soluble silicate,[65, 66, 67] but adhesives of this type have come into extended use as the result of studies from 1917 to 1921 by U. S. Forest Products Laboratory, induced by the need of water-resistant glues for airplane construction. This work eventuated in a patent to S. Butterman[68] which was assigned to the United States Government and dedicated to the public. Butterman's adhesive proved more satisfactory than any of its predecessors and has

* *Cf.* page 239.
[65] Pick, Ger. Pat. 60,156 (1891).
[66] Wenck, Ger. Pat. 116,355 (1900).
[67] Jeromins, Ger. Pat. 154,289 (1904).
[68] Butterman, S. S., U. S. Pat. 1,291,396 (Jan. 14, 1919).

been extensively used. The original formula was modified by increasing the lime to add water-resistance, and the following, known as 4B, is the basis of practice in many industrial plants as a water-proof glue for wood.[69, 70]

	Parts by Weight
Casein	100
Water	200–230
Hydrated lime	20–30
Water	100
Sodium silicate	70

Method of Mixing Casein Glues.[71] Attention must be given to the technic of mixing this or other casein glues if success is to be had. Dry casein is first soaked in water for 15 minutes, then hydrated lime and water are mixed separately and added to the casein with a mechanical agitator in operation at 50-60 revolutions per minute. After two or three minutes the silicate solution is put in and the mixing continued for half an hour. It is necessary to determine by test what amounts of water to use for a particular casein and to reject any batches which are too thick or too thin, rather than to attempt much adjustment after they are made up.

TABLE 84.

Natural sour casein takes.................	130–170 parts water
Mineral acid casein takes.................	170–200 parts water
Rennet casein takes.......................	about 280 parts water

Various alkaline salts are able to extend the working life of casein glues but the silicates are the most effective as shown by Browne's graph reproduced herewith.[72] (Fig. 124.)

The water-resistance of these glues appears to be due to reaction between calcium hydroxide and casein.[73] Dolomitic limes may be used if proper allowance is made for their calcium content. Water-resistance increases up to 30 parts high-calcium lime and then falls off with further additions. The reaction proceeds rapidly unless controlled by the addition of silicate, which greatly extends the time during which the glue remains in a workable condition. 4B formula gives a glue which has a working life of six to twenty-four hours.[74]

[69] Prestholdt, Henry L., U. S. Pat. 1,604,311, 1,604,313, 1,604,317 (Oct. 26, 1926).
[70] Bogue, R. H., *Chem. Age,* 30, 3, 103-6 (1922).
[71] Dunham, Andrew A., U. S. Pat. 1,391,769 (Sept. 27, 1921).
[72] Sutermeister, Edwin, "Casein and Its Industrial Applications," New York: The Chemical Catalog Co., Inc., American Chemical Society Monograph Series, 1927.
[73] U. S. Dept. Agr., Rep. No. 66, "Glues Used in Airplane Parts," 1920.
[74] Dunham, Andrew A., U. S. Pat. 1,391,770 (Sept. 27, 1921).

For some purposes it may be best to make a glue with less than the optimum amount of lime for water-resistance. This will have longer working life and its water-resistance may be enhanced by the method given below.
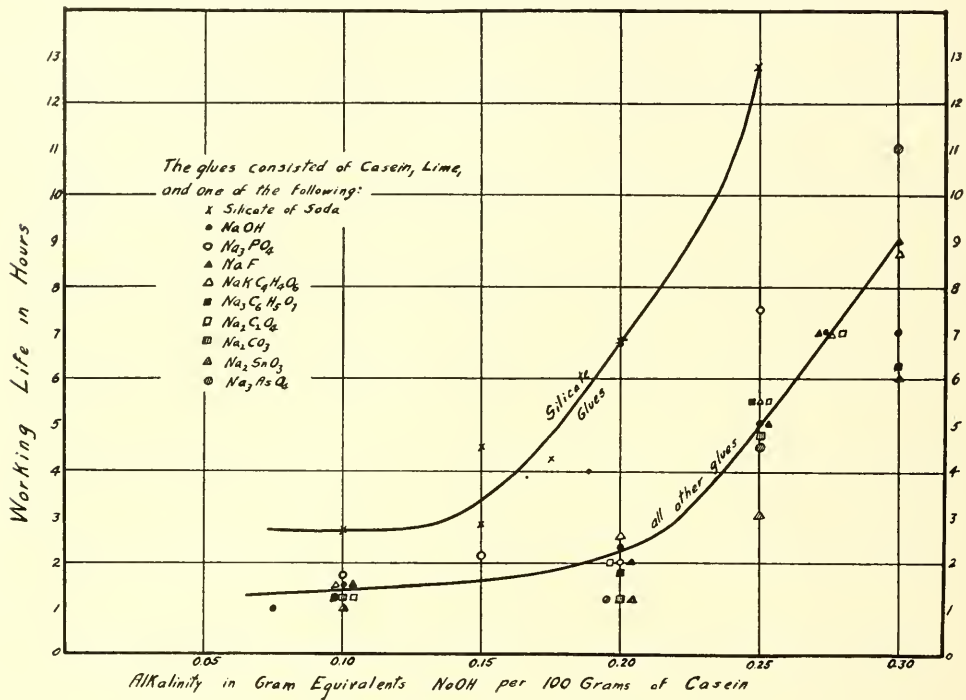
FIG. 124.—Influence of Alkalinity of Casein Glues on Their Working Life.

Casein Glues and Heavy Metal Salts. It was found possible to increase the water-resistance of these glues by adding copper salts,[75, 76] and some other soluble salts of heavy metals perform similar service.[77] The explanation of this behavior is not known but it increases the permutations by which these glues can be adapted to longer or shorter working life.

The glue known to the Forest Products Laboratory as No. 11 embodies this idea as follows:

Casein	100
Water	220–230
Hydrated lime	20–30
Water	100
Silicate of soda.......................	70
Cupric chloride	2–3
Water	30–50

[75] Butterman, S., and C. K. Cooperrider, U. S. Pat. 1,456,842 (May 29, 1923).
[76] Jones, W. L., "Improved Casein Glue Containing Copper," 8, 4477 (1922), Madison, Wis.: Forest Products Laboratory.
[77] Henning, S. B., Can. Pat. 226,535 (1922).

The procedure in the first three steps is the same as for 4B. The mixture is brought to a smooth consistency after the silicate is added; then the solution of cupric chloride or an equivalent amount of sulfate is added slowly with stirring. It tends to form lumps, but these disperse to make a smooth violet-colored adhesive of excellent water-resistance.

Silicate solutions may be added to thicken or reduce the cost of glues made from casein and caustic soda.[78] These are strong but without great water-resistance.

Properties. Casein-lime-silicate glues make joints on wood which
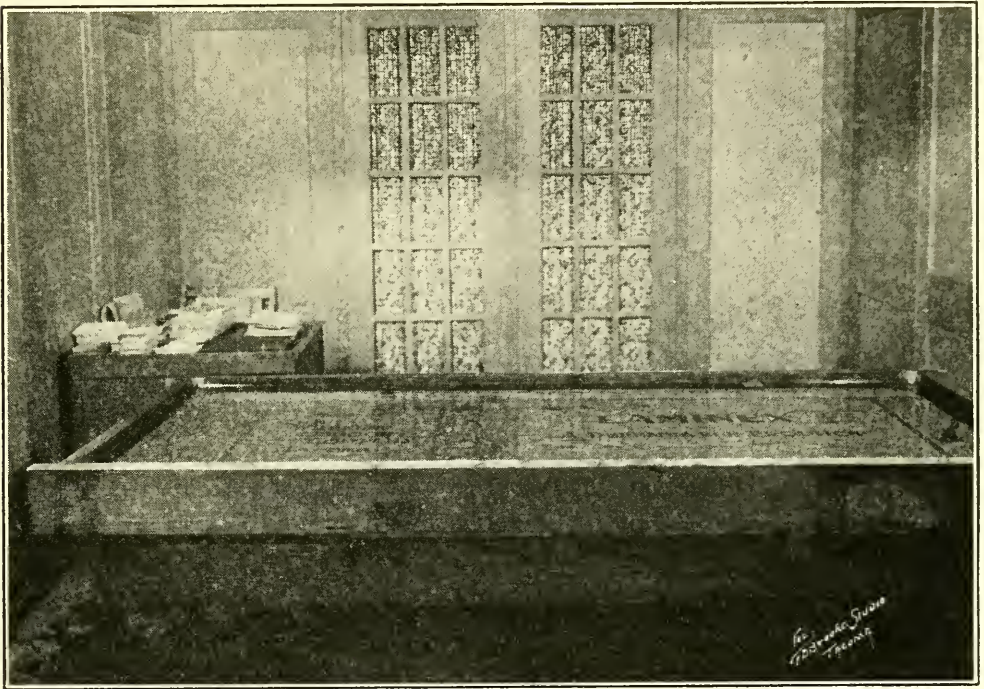
FIG. 125.—Plywood Door in Water Soaking without Damage.

are stronger than the wood fiber. They will stand prolonged immersion in water or even boiling. They have somewhat greater tendency than animal glues to dull knife edges of woodworking tools, but can be easily sawed. Among the many combinations possible it appears that casein glues free from lime and containing silicate can be produced with a high degree of water-resistance, but the technic of their manufacture has not been divulged. They are said to have no more effect on cutting tools than the wood itself.

[78] "Casein Glues, their Manufacture, Preparation, and Application," Madison, Wis.: Forest Products Laboratory, revised July, 1923,

The spread and hence the cost of these adhesives will depend upon working conditions. A thick quick-setting glue will obviously not spread as far as a thinner glue which, containing more silicate, may remain in working condition for several days. Thirty square feet of three-ply panel per pound of dry casein is easily attained.

Substitutes for Casein. A product of lower adhesive strength but otherwise comparable has been made from condensed buttermilk.

Vegetable proteins offer an attractive source of cheap water-resisting adhesive. Soya bean meal [79] has been used and with suitable allowance for its individual characteristics yields a strong water-resistant glue with a wet mix using lime and silicate solution. Other press cakes from oil-bearing seeds, such as peanut and cottonseed, are susceptible to similar treatment.[80]

Dry Mixtures. Various dry mixtures containing casein and solvent are on the market. Most of them can be extended and reduced in cost by adding silicate as the final step to the wet mixture, but attempts to use soluble forms of silicate in the dry mixture have had very limited use.

It is usually possible to make a better glue from the same casein by observing the sequence of steps specified in formula 4B or with the addition of heavy metal salts as in formula 11, than by attempting to use a mixture which contains protein, solvent, and lime, all coming into contact with water at the same time. Dry mixtures generally require more solvent, which does not add to adhesive strength or water-resistance but is only a means of bringing the protein into condition to spread and should, therefore, be kept to a minimum.

A dry product described by Bogue [81] is made by dissolving gum arabic in a silicate solution, 1 part of gum in 5 parts 1.38 specific gravity (40° Baumé) Na_2O, $3.3SiO_2$ evaporated to dryness and ground. This is a difficult procedure.

Gum-silicate mixture	50 mesh	20 parts
Casein	40	40
Calcium hydroxide	150	25

This is to be made up with 45 parts of dry mix in 100 parts water, or the following for a wet mixture with gum arabic:

Casein	47
Calcium hydroxide	29.5
Silicate	15.5
Gum arabic	8

[79] Johnson, Otis, U. S. Pat. 1,460,757 (July 3, 1923); reissued 16,422 (Sept. 14, 1926).

[80] Osgood, G. H., U. S. Pats. 1,601,506, 1,601,507 (Sept. 28, 1927).

[81] *Chem. Age,* 30, No. 3, 103-106 (1922).

It is obvious that many other minor ingredients can be used to modify the character of these adhesives, as glycerin, shellac, rubber latex, and a large number of earthy materials.[82, 83]

Blood Adhesives.

Wood's Glue. Blood adhesives set by heat which coagulates the albumin are among the most resistant to water. They also may be made up with silicate solutions. Wood [84] calls for:

1 gallon saturated solution of silicate of soda (presumably $Na_2O, 3.3SiO_2$ 1.38)
2 gallons blood
3 gallons water
0.1 ounce ammonia water (if quick drying is desired)

Good results may be obtained when the ingredients are varied in amounts as much as 20 per cent. Heating is carried on at temperatures not less than 65°C. nor more than 93°C. This mixture, when used to join two surfaces, dries and hardens to be waterproof within twenty-four hours without applying heat to the surfaces.

Haskell's Glue. Another glue of this type is that of Haskell.[85, 86] To 45 parts blood albumin and 55 parts water, 9 per cent of sodium silicate based on albumin is added and mixed until the mass is a homogeneous syrup. The specification does not make clear the exact character of the silicate to be used. It is believed, however, that Na_2O, $2.9SiO_2$, specific gravity 1.48, was intended.

Glue-Silicate Mixtures.

There are many adhesive mixtures in which silicates occur as minor ingredients along with glue. Glue hydrolized with silicate solutions is said to be stronger but more brittle than that hydrolized with sodium hydroxide. This may be overcome by adding glycerin but the film is thus made hygroscopic.[87] An example of the complicated mixture with glue is that of Tsukoski,[88, 89] which calls for: gliopeltis furcata, glue, sodium silicate, potassium dichromate, alcohol, lead oxide or lead acetate.

[82] Isaacs, M. R., U. S. Pat. 845,791 (March 5, 1907).
[83] Dance, Edward L., U. S. Pat. 1,478,943 (Dec. 25, 1923).
[84] Wood, W. W., U. S. Pat. 1,270,477 (June 25, 1918).
[85] U. S. Pat. 1,516,567 (Nov. 25, 1924).
[86] Drushel, W. A., U. S. Pat. 1,476,805 (Dec. 11, 1923).
[87] Tressler, D. K., personal communication.
[88] Jap. Pat. 38,763 (June 1, 1921).
[89] Bottler, Max, *Kunstoffe*, **15**, 89-91, 114-117 (1925).

Various substances which are compatible with silicate solutions may be used to modify the character of adhesive films which are primarily composed of silicate as well as those which are more complex.[90-94] The permutations of the mixtures are infinite. Gum arabic has already been mentioned. Other water-soluble gums can be employed. Gum shellac can be dispersed in silicate solutions with or without the aid of ammonia. Glycerin is a favorite means of retarding drying and thus retaining a degree of flexibility not inherent in the silicate film. Mal-
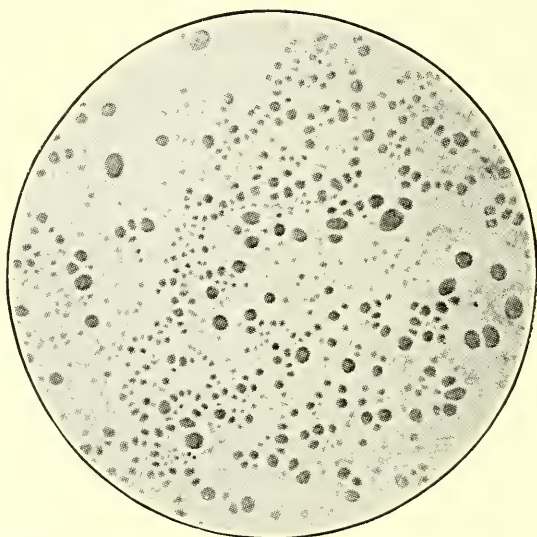
FIG. 126.—Rubber Latex Particles Suspended in Silicate Solution. Magnified 1200 Times.

colmson extended silicate solutions without loss of viscosity by mixing them with sodium chloride brines.

Rubber latex stabilized with ammonia mixes readily with adhesive silicate solutions, softening and increasing the flexibility of the film.[95-97] It also increases somewhat the resistance to water, but being a discontinuous material, it cannot protect the silicate entirely from the action of water.

Sugar can also be used.[98] Commercial glucose syrup mixes in the

[90] Malcolmson, J. D., U. S. Pat. 1,379,639 (May 31, 1921).
[91] Dahse, W., Ger. Pat. 318,516 (Aug. 23, 1918).
[92] *J. Soc. Chem. Ind.,* **39,** 517A.
[93] Meta, Sarason, Ger. Pat. 316,080 (Nov. 13, 1919).
[94] Besele, Lynaz, Ger. Pat. 61,703 (1892).
[95] *"Silicate P's & Q's,"* **5,** No. 5, Philadelphia, Pa.: Philadelphia Quartz Company, **1925.**
[96] Teague, M. C., U. S. Pat. 1,550,466 (Aug. 18, 1925).
[97] See also, Harris, John, U. S. Pat. 1,631,265 (June 7, 1927), which is a modification of U. S. Pat. 1,498,270 (June 17, 1924).
[98] Hacket, William, Brit. Pat. 20,528 (1900).

cold with adhesive silicates but reacts and causes gelation when heated. Many hydrolized products such as corn cob adhesive are miscible.[99, 100] Waste sulfite liquors and vegetable tanning extracts can be mixed after a pretreatment with sodium hydroxide.

Testing Adhesives.

The art of making and using adhesives has not yet advanced to a point where results can with safety be predicated from tests other than those which simulate the conditions of service. Except in the cases of a few materials which have been intimately studied, as glue, and starch, we must rely on actual measurements of bond strength with variations of moisture, setting time, or other factors of import in the industrial processes concerned. The older literature pays little attention to the evaluation of adhesives and the more recent is specific to the arts concerned. Wood-gluing, because it makes maximum demand on adhesive strength, has had the most attention; but even here the practice of industry is only beginning to be systematic. Much is to be expected when more complete and comprehensive studies of adhesives have been made.[101-105]

General References

General references on adhesives in which references are made to soluble silicates are given below.

Breuer, Carl, "Die Kitte und Klebstoffe," Leipzig: Dr. Max Jänecke, Verlagsbuchhandlung, **1922.**

Kausch, "Adhesives and Binding Materials," *Kunstoffe,* 3, 63-66, 89-92, 110-112, 127-130 (1913).

Allen and Truax, "Glues Used in Airplane Parts," U. S. National Advisory Committee for Aeronautics, Report No. 66 **(1920).**

Standage, H. C., "Agglutinants of all kinds and for all purposes," London: Archibald Constable & Co., Ltd., **1907.**

Scherer, "Casein: Its Preparation and Technical Utilization," London: Scott, Greenwood & Co., **1911.**

Furness, Rex, *J. Soc. Chem. Ind.,* 41, 381R-384R.

Sutermeister, Edwin, "Casein and Its Industrial Applications," New York: The Chemical Catalog Co., Inc., American Chemical Society Monograph Series, **1927.**

[99] LaForge, F. B., U. S. Pat. 1,285,249 (Nov. 11, 1918); *Fibre Containers,* 6, 38-40 (1921).

[100] Sweeney, O. R., *Iowa State College of Agriculture,* Bull. 73, 23, No. 15 (1924).

[101] Elmendorf, Armin., *Proc. Am. Soc. Testing Materials,* 20, 324 (1920).

[102] Forest Products Laboratory, Technical Notes: "Effect of Age on Casein Glues," Lo-11, 377, No. F-18, and "Method of Testing Strength of Joint Glues," Lo-11, 320, No. F-16.

[103] Wagner, H., *Farben-Ztg.,* 31, 2132 (1926); *Brit. Chem. Abstracts,* 45, No. 32, 638 (1926).

[104] "Second Report of the Adhesives Research Committee," Dept. Sci. Ind. Research, London: His Majesty's Stationery Office, **1926.**

[105] Vail, James G., *Fibre Containers,* 6, No. 9, 16 (1921).

Chapter IX.

Sizes and Coatings.

THE NATURE OF SILICATE FILMS.

PROPERTIES OF SILICATE FILMS.

Just as many a prospector has found pyrite and imagined it to be gold, so great numbers of experimenters have found that silicate solutions produce a beautiful, transparent, and colorless film, and have regarded it as a new mineral varnish, not only cheaper, but with outstanding advantages over the materials hitherto used. These silicate films would be incombustible and odorless; the supply would be unlimited; the solvent for reducing them would be water.

Silicate solutions do, in fact, produce handsome films; but they have three inherent limitations: they are slowly soluble in water; they absorb carbon dioxide from the air, and tend to lose their pristine beauty by efflorescence; they lose water and become brittle, which eventually means they become discontinuous.

There are means of limiting the effect of these undesirable characteristics, so that even though the silicates can never be the universal coating medium of which inventors have dreamed they yet serve to make films of considerable importance in industry.

EFFECT OF RATIO.

Beginning with $Na_2O,4SiO_2$, we obtain colloidal solutions characterized by the ability to set very rapidly by the loss of small amounts of water. A 35 per cent solution assumes the appearance of dry varnish when it has lost 10 per cent of its weight of water. This film is least affected by moisture or carbon dioxide, and it passes most quickly through a crumbling stage to brittleness.

As the alkalinity increases, the setting time is lengthened, the solubility and ability to take up carbon dioxide is increased, and water is held more firmly, extending the period in which the film may be bent without cracking.

When the last solution which retains its colloidal character under

all ordinary conditions (Na_2O, $1.5SiO_2$) is reached, setting takes place only in a dry or warm atmosphere; solubility is high and the film instead of being gelatinous is sticky. Its ultimate disintegration is more likely to be due to crystallization of sodium carbonate than to the brittle character which results from dehydration.

Procedure to Offset Limitations.

The best means of counteracting solubility of silicate films is to cover them with water-resisting media or to cause the colloidal silicate to be protected by the formation of an insoluble gel. This is brought about by securing the presence of a suitable amount of metastable silica which gels when water is evaporated. The latter may be prepared by neutralizing a part of the silicate solution with acid and preventing immediate gelation by the addition of more silicate. The gel forms when the film begins to evaporate.[1] This is more fully treated in the chapter on gels. Materials with which silicate films may be overlaid are paraffin, chlorinated naphthalenes, rubber solutions or latex, waxes, gum solutions, nitrocellulose lacquers, or other colloidal films which are not easily saponified.

Films which are laid upon a surface to alter its properties are subject to the same sort of modification as adhesive films. They may be mixed with suitable colloids to alter their character. Starch, glycerin, and rubber latex are the most useful. It is obvious that any adhesive can also be used as a sizing agent, but the reverse is not true since the sizing agent often lacks adhesive properties.

Uses of Silicate Films Without Pigment.

Coating Papers.

Method of Application. Manila or chip board for making cartons to contain coffee or condiments is much more permeable than the metal containers which were formerly used. Its resistance is improved by a silicate coating. Na_2O, $3.3SiO_2$ or $Na_2O,4SiO_2$ are adapted for coating paper. They are spread very thin with steel rolls for smooth papers, or with rolls covered with rubber for papers of uneven surface. The amount of silicate on the basis of 1.38 specific gravity for Na_2O, $3.3SiO_2$ varies from 9.81 kilos per 1000 square meters of surface to 98.1 kilos (two pounds per 1000 square feet to about 20 pounds). To make a light coating under paraffin, 24.6 kilos per 1000 square meters (five pounds per 1000 square feet) is a fair average amount.

[1] Vail, James G., and John D. Carter, U. S. Pat. 1,129,320 (Feb. 23, 1915).

Silicate films as thin as these, when spread upon a porous surface like paper, set very rapidly. It is usual to run coating machines at two hundred linear feet per minute and to have the silicate film dry enough to permit a final coat of paraffin within about 9 meters (30 feet), i.e., within ten seconds. This is important as paraffin will not properly wet a moist surface but will "crawl" unless the silicate seems dry to the touch. The speed will depend somewhat upon atmospheric conditions

Fig. 127.—Cartons Sized with Silicate.

and upon the moisture in the paper. Concentration of the silicate and also machine conditions must be adjusted to compensate for changes of humidity and temperature. Thus a specific gravity of 1.32 may be right for dry warm weather, but a somewhat higher specific gravity with a closer set of the spreading roll may serve better when it is cooler or more humid or when the paper is not as dry as it should be. As the viscosities of the silicates have an important bearing on this use, $Na_2O,4SiO_2$ must be run at a lower concentration than the more alkaline grades. It sets faster, but this advantage is offset by greater sensitiveness of viscosity to temperature changes.[2]

Grease-proofing. It has been asserted that soluble silicates are not adapted to grease-proofing paper. As applied to perfect resistance, such as sheet metal gives, this is true, for the silicate film develops hair cracks in time. The following tabulation showing the time required for grease to penetrate silicated cartons in comparison with plain patent

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[2] *Paper*, **22**, 358 (1919).

coated stock and plain double-lined manila shows the different behavior of various oily foodstuffs as well as different cartons.[3, 4]

TABLE 85. *Time in Days Required for Penetration of Grease.*
(Each figure is the average of 5 tests.)

	Silicated Cartons	Plain Patent Coated	Plain Double Manila Lined
Prepared flour No. 1.............	160	21	4
Prepared flour No. 2.............	41	30	13
Shredded coconut	79	3	2
Peanuts	5.5	1	1
Chocolate wafers	270+	146	104

Extensive studies have shown that silicated stock is very useful in keeping crackers and biscuits fresh. This is due to the fact that passage of moisture through the board is delayed. Silicates of soda are soluble in water but the untreated paper acts like a wick and the silicate coating stops this action almost completely. Oil-bearing materials differ greatly in penetrating power and many products which would quickly go through untreated paper are held by silicate films.[5, 6]

It has also been found that the aroma of coffee and spices is better retained in a package made from silicated stock.[7] Using silicate under paraffin serves a double purpose. It prevents the softening of the fiber stock by partial saturation with paraffin, and it also reduces the amount necessary to make a continuous film. The double-coated board is largely used to contain soda crackers or other baked products which contain little oil but are kept fresh in a dry package. Additions of finely divided fillers, such as mica and aluminum bronze, which take the form of flakes, help to make grease-resisting films with silicate solutions.[8]

Modifications. Silicate-lined paper cartridges were used by Van Meter[9] as reaction chambers for generating poisonous gases from solid charges and chlorine. Surface sizing of paper has been done with a large number of mixtures with silicate as one constituent. A great variety of coatings suited to specific needs can easily be worked out

[3] Research Report, Folding Box Manufacturers Assoc.
[4] "*Silicate P's & Q's,*" **5**, No. 10, 1925; Philadelphia, Pa.: Philadelphia Quartz Company.
[5] Artus, W., *Chem. Zentr.*, **28**, 749 (1857).
[6] Ellis, C., U. S. Pat. 1,311,595 (1919).
[7] Vail, James G., *The Spice Mill*, **47**, 134-136 (1924).
[8] Cavanaugh, A. J., Jr., U. S. Pat. 1,357,844 (Nov. 2, 1920).
[9] Van Meter, James W., U. S. Pat. 1,419,653 (June 13, 1922); U. S. Pat. 1,430,772 (Oct. 3, 1922); U. S. Pat. 1,654,025 (Dec. 27, 1927).

when the properties and compatibilities of silicate solutions are under-stood.[10, 11, 12]

Among these may be mentioned the process of Wezel,[13] who uses horn shavings dispersed with sodium hydroxide and adds a silicate solution, and a process of making paper water-resistant by using a strongly silicated soap solution on a surface previously prepared with lead acetate and zinc oxide in a mixture of starch and gum arabic.[14, 15]

Metallic films made from foil laid on a silicate film or deposited from solution upon a silicated surface have been proposed.[16, 17]

For Memorandum Pads. A silicate coating on bleached paper of high grade or on bristol board is used for memorandum pads. The silicate surface is easily written on with a pencil and as easily erased by rubbing with a moist cloth. The operation may be often repeated before the film ceases to be effective. Bleached fiber is chosen for this purpose to avoid discoloration in contact with the alkaline film.

BARREL TESTING AND SIZING.

Distinction Between Testing and Sizing. Wooden containers for fats and oils must be treated to overcome their natural porosity. The practice of the industry involves two steps. The first is to test the tightness of a barrel or cask soon after it is set up, and the second is to apply a lining or sizing coat near the time when it is to be filled. Bone glues, pitch, and casein serve under some circumstances; but silicates of soda are almost universally used for edible oils, lard, and hydro-genated fats shipped directly in wooden vessels.[18]

Many barrels for mineral oil are also silicate-sized, and a still larger number are tested with silicates over which a sizing of glue may be put on.

Method for Testing. Testing is conducted by putting a gallon or more of hot $Na_2O, 3.3SiO_2$ diluted to about 1.1 specific gravity into the barrel, closing the bung hole and turning the barrel about till the liquid covers the entire inner surface. This procedure heats the air and makes a pressure within, which drives the liquid into any small openings,

[10] Morrison, F. J., U. S. Pat. 1,365,715 (Jan. 18, 1921); *Papier,* 22, 358 (1919); *C. A.,* 14, 627.
[11] Kojima, Yonejiro, Jap. Pat. 42,365 (April 20, 1922); *C. A.,* 18, 470.
[12] Crowell, Charles H., U. S. Pat. 1,577,450 (March 23, 1926).
[13] U. S. Pat. 686,374 (Nov. 12, 1901).
[14] Sekiya, Keiya, Jap. Pat. 41,392 (Jan. 12, 1923); *C. A.,* 17, 2645.
[15] Menzel, K. C., and Paul Meyerburg, Ger. Pat. 405,299; *Papierfabr.,* 22, 573-4 (Nov. 30, 1924).
[16] Marino, Pascal, Brit. Pat. 20,012 (Jan. 11, 1912).
[17] Diamond Decorative Leaf Company, Brit. Pat. 186,889 (June 14, 1923).
[18] Batchelder, James H., U. S. Pat. 900,256 (May 5, 1908).

whence it exudes with a hissing sound which is easily detected. A peg driven into a worm hole is adhesively fastened in place. Some porous parts of the wood are closed by the silicate itself, and the cooper knows when his work is water-tight. The bung is now removed and the excess liquid returned to the heater for further use. One-half pound of silicate solution, specific gravity 1.38, is needed per 50 gallon barrel for testing, though some kinds of wood will absorb more than others.
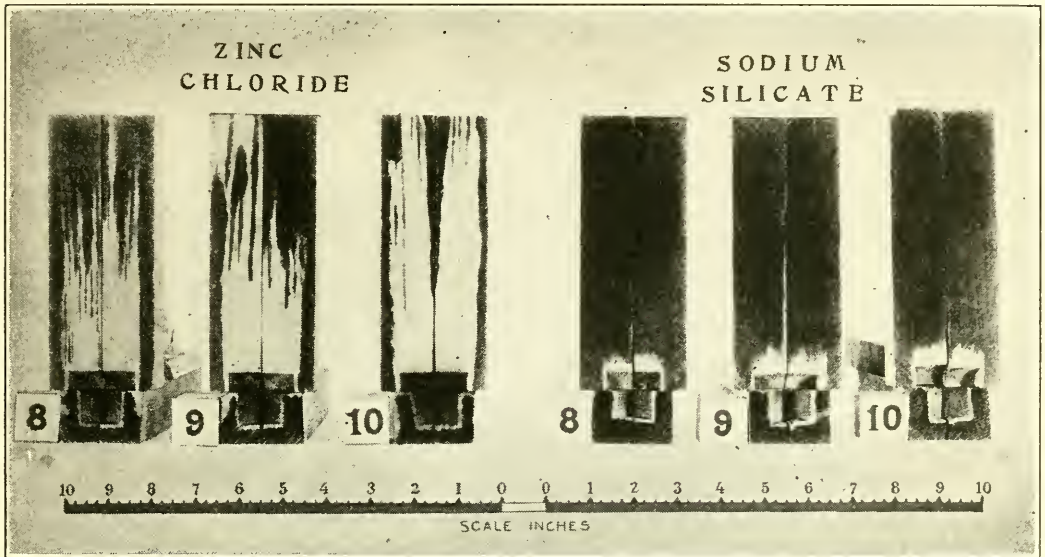
Fig. 128.—Comparative Penetration of $ZnCl_2$ and Na_2O, $3.3SiO_2$ into Hemlock. (Courtesy of Forest Products Laboratory.)

It is noteworthy that sound wood excepting those varieties which, like oak, have natural canals of considerable size is not easily penetrated by silicate solutions. Hemlock test pieces put into a vessel from which the air was exhausted, then covered with silicate solutions and subjected to 50 pounds pressure while immersed, showed a penetration of only an eighth of an inch from the sides and less than half-an-inch from the ends. Another experiment shown in the cut illustrates the great difference in penetration when attempts were made to saturate wood with $ZnCl_2$ and Na_2O, $3.3SiO_2$.[19] The testing treatment is therefore primarily a means of seeking out and closing actual channels through or between the pieces of which the barrel is made.

Method for Sizing. The sizing coat is made with silicate of higher concentration. It is well to choose conditions which will not leave a thick covering on the wood. The saw marks on the inner part of the

[19] Teesdale, Clyde H., *Fifth Progress Report*, **L-177**, Forest Products Laboratory, Madison, Wis.

barrel should be easily located with the fingers after sizing. Although the silicate does not penetrate deeply, thin films do derive a substantial measure of protection from intimate contact with wood fiber in barrel sizing. Thirty-five degrees Baumé, 1.32 specific gravity, is right for $Na_2O, 3.3SiO_2$ under average conditions. It should be heated to 82°C. (180°F.). Enough liquid should be put into the barrel to make a substantial pressure; five gallons is not too much. This will also insure heating the staves and the excess liquid can be completely drained out. A few accidents are on record in which the pressure has risen to a point

Fig. 129.—Silicate Sizing Barrels.

sufficient to blow out the head of the barrel. If too much pressure develops, it is better to lower slightly the temperature and concentration of the silicate rather than to reduce the amount put in at each operation because imperfect drainage is a source of trouble and the larger amount of liquid cools more slowly. The amount of silicate (40° Baumé basis) required for this treatment will vary from 1½ to 5 pounds per 50 gallon barrel, depending on the porosity of the wood and the manner of handling.

It is important to control the concentration of the silicate supply in the heater because hot silicate evaporates and the barrel takes up water as the film sets. Also the return of solution drained from the barrels involves exposure and concentration to a surprising degree.

Draining is accomplished by placing the packages with the bung hole at the lowest point over the return trough. It should be continued as long as there is any flow, thirty minutes at least. Spray machines are also used for silicate sizing.

Silicate sets more rapidly than glue in the badly ventilated interior of

a barrel. $Na_2O,4SiO_2$ has been used experimentally. It sets more rapidly than the usual material but requires much more care, due to its rapid rise of viscosity with concentration. This has thus far prevented its adoption, although its lower solubility and alkalinity make it attractive.

Open wooden vessels, such as lard or butter tubs, are best sized by filling them full of hot silicate solution and allowing them to stand ten minutes or more before draining.

Conditions for Use. Oils, whether animal, vegetable or mineral, with viscosities above 150 centipoises may be satisfactorily held in sili-
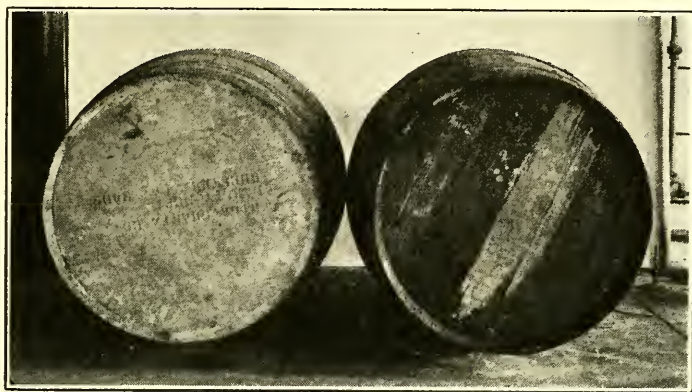
Fig. 130.—Penetration of Turpentine through Wooden Barrel Head. Left, Silicate Tested, Glue Lined. Right, Glue Tested and Lined.

cate-sized containers. Lighter mineral oils are better put into barrels tested with silicate and lined with glue, which is more elastic and more costly. Turpentine barrels thus prepared have been shown to hold better than glue-tested barrels but as turpentine is clouded by contact with silicate the practice is not considered advisable.

Vegetable oils containing free fatty acid make it necessary to be careful that the silicate film is well dried before coming in contact with oil. If this is done, no appreciable reaction takes place. If a little wet silicate remains, the oil is likely to be clouded by a slight saponification. This has happened also to barrels which were properly sized and filled but not painted on the outside when they have lain awash in the hold of a ship. Under these conditions enough water entered the wood to dissolve the silicate somewhat and cloud the oil.

Time for Sizing. As the silicate film is subject to deterioration if long exposed to the air without the protection of the oil, the sizing should not precede filling by more than about ten days, although the circulation inside a barrel is poor and the film remains intact longer than it would were it exposed outside. In some plants drying is hastened

by inserting a pipe to draw out air or blow in a warm current. This is good practice. Unless so treated, glue sizings are prone to mold in hot, damp climates, where a week may be necessary to dry the coat properly without forced circulation. Though the silicate sets faster than glue and does not nourish molds, better films are formed when drying takes place within a few hours. The drier the film, the slower will be the absorption of carbon dioxide.

Fire-Proofing.

Character of Protection. Von Fuchs coated theatrical scenery [20] in Munich in 1820, and since that time there have been numerous cases in which silicate solutions were used to prevent fire.[21-37] This use depends upon the presence of a film which is incombustible. It cannot give much protection to combustible materials after temperatures capable of releasing inflammable gases by distillation are reached. When the film consists of a silicate containing a substantial amount of water, additional protection results from its property of intumescence. When rapidly heated above the boiling point of water, steam is driven off with sufficient energy to blow bubbles in the now liquid film and these as a result of the concentration solidify, making a porous mass which is an excellent thermal insulator.[38] So long as the film retains its

[20] Krätzer, Hermann, "Wasserglas und Infusorienerde," Hartleben's chemisch-technische bibliothek, **2**, Wien, **1907**.

[21] Andés, Louis Edgar, "Feuersicher-, geruchlos- und wasserdicht-machen aller materialen, die zu technischen und sonstigen zwecken verwendet werend," **222**, Wien: Hartleben's chemisch-technische bibliothek, **1896**.

[22] *Verhandlungen des Vereins zur Beförderung des Gewerbfleisses in Preussen*, **20**, 49-53 (1841).

[23] Eschenbacher, August, "Die Feuerwerkerei; oder, Die Fabrikation der Feuerwerkskörper," **11**, 3rd ed., Wien: Hartleben's chemisch-technische bibliothek, **1897**.

[24] *Neueste Erfindungen und Erfahrungen*, **40**, 566-567 (1913).

[25] Hexamer, C. J., *J. Franklin Inst.*, **147**, 65-70 (1899).

[26] Kaiser, C. G., *Poly. J.*, **21**, 91-92 (1826).

[27] Koller, Theodor, "Die Imprägnirungs-Technik," **219**, Wien: Hartleben's chemisch-technische bibliothek, **1896**.

[28] Sandham and Abel, *Mechanics' Magazine*, **67**, 531-532, 580-582, 609-610 (1857). Same, abstract, *J. Franklin Inst.*, **68**, ser. 3, **38**, 284-285 (1859). Same, condensed translation, *Poly. J.*, **149**, 194-197 (1858). Same, abstract translation, *Bull. soc. d'encour. l'ind. nat.*, **58**, ser. 2, **6**, 374-375 (1859).

[29] Pätsch, Albert, *Z. ver. deut. Inge.*, **9**, col. 543 (1865). Same, *Poly. J.*, **177**, 492 (1865). Same, abstract, *Chem. Zentr.*, **36**, n.s.v. 10, 944 (1865).

[30] *Allgemeine Bauzeitung*, **5**, 36-38 (1840).

[31] Ellery, James B., U. S. Pat. 1,435,957 (Nov. 21, 1921).

[32] Hess, Henry K., U. S. Pat. 1,344,891 (June 29, 1920).

[33] Hopkins, N. M., U. S. Pat. 1,507,181 (Sept. 2, 1922).

[34] Tumminelli, Arcangelo, U. S. Pat. 1,126,132 (Jan. 26, 1915).

[35] Scharwarth, John A., U. S. Pat. 1,136,370 (April 20, 1915).

[36] Harris, James E., U. S. Pat. 1,612,506 (Dec. 28, 1926).

[37] Ashenhurst, Harold S., U. S. Pat. 1,353,621 (Sept. 21, 1920).

[38] Arthur, W., *loc. cit.*, U. S. Pat. 1,041,565 (Oct. 15, 1912).
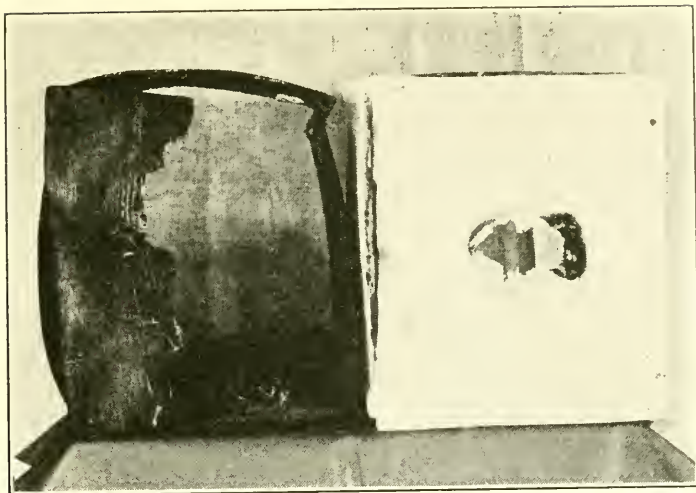
FIG. 131.—Effect of Silicate Paint on Yellow Pine, Exposed to the Flame of a Meker Burner.

vitreous appearance, and contains water, which will be the case if it is air dried, it is able to swell when heated and thus to delay ignition
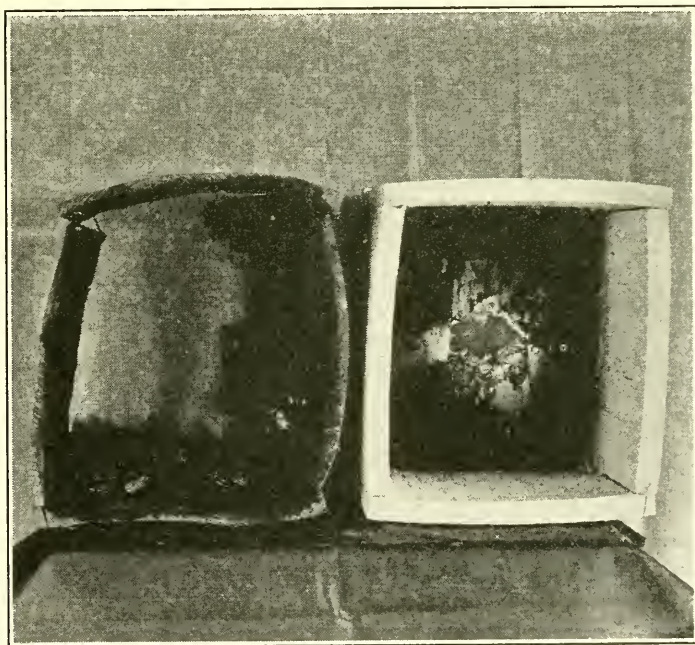
FIG. 132.—Same as Figure 131. Viewed from Under Side.

from minor sources of heat such as sparks, flashes of flame, or even small continuing fires such as might result from the ignition of a small leak in a gas conductor. Intumescence is reduced by the introduction of pigment.

The two boxes shown in Figures 131 and 132 give the comparison between yellow pine, untreated, and treated with silicate paint.[39] Each was exposed to the flame of a Meker burner, which burned a hole through the painted wood. The flame did not spread, but passed through the hole for more than an hour, leaving the main body of the wood unaffected. The untreated wood ignited promptly and would have been completely consumed had not the fire been extinguished.

The problem in designing applications of silicate solutions for fire protection is to circumvent the failure of the film by carbonating. This may be done by covering and thus reducing exposure, or for hazardous factory operations the coating may be renewed at intervals.[40]

Protection of Timbers. Timbers of certain railway tunnels have been cheaply protected by spraying them with $Na_2O, 3.3SiO_2$, 42° Baumé and immediately throwing against the wet silicate fine sand which adhered and yielded a silicious coating very resistant to flame or sparks. Slaked lime has been used in the place of sand and gives the advantage of early insolubility. Similar treatment has been applied to timbers in mines. Another method is to allow the silicate coating to dry and then spray with aluminum sulfate.

Protection of Rubber Insulated Wire. Rubber insulated wire used in the telephone industry is less liable to burn when a silicate film is interposed between the rubber insulation and the outer braided covering of cotton protected with fire-resisting salts. The extent of protection is reduced by long exposure but is almost complete for the first year.

Silicate-saturated felts have been laid between double wooden floors of tongue and groove type and this protective measure has been recognized in building codes.[41] $Na_2O, 3.3SiO_2$ is usually preferred for making fire-resisting coatings.

Protection Against Light Oil Fires. As an example of fire-resistance of a film containing pigment, the illustration of a corrugated paper box coated inside and out with $Na_2O, 3.3SiO_2$, specific gravity 1.18 containing calcium carbonate and lithopone, will serve. The dimensions were $4'' \times 4'' \times 12''$. One hundred cc. of petroleum distillate, 50° Baumé light, were put into the box and ignited, the flames rising around the outside of the second box. The heat was sufficient to char

[39] Gardner, Henry, *Bull.* No. 4, *Paint Mfrs. Ass., Sci. Sec.* (1914) ; *Drugs, Oils, and Paints,* **29,** 10, 370 (1914).
[40] Pätsch, *loc. cit.*
[41] City of Boston Building Laws, Chapter 550, Section 32, page 103, amended under Acts of 1907.
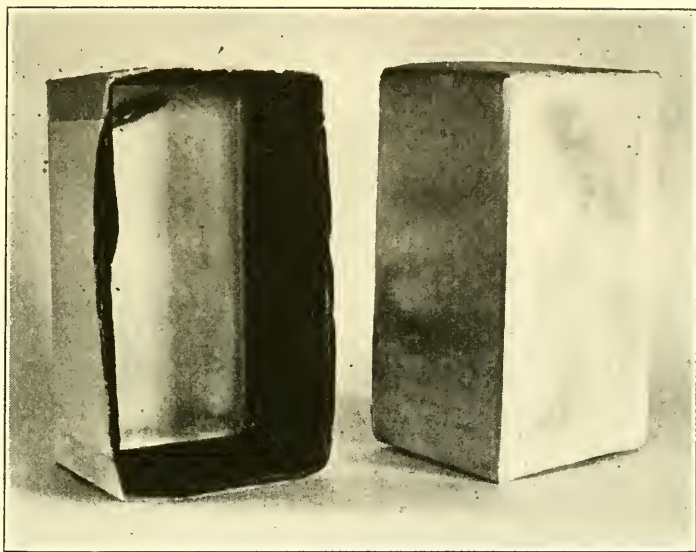
Fig. 133.—Corrugated Paper Box Flame-proofed with Silicate Paint.

the paper nearest the fire but the other paper sheet was uninjured and the box was not ignited.

Mixtures for Fire-Proofing. Numerous compositions of matter involving soluble silicates have been patented as fire-proofing agents. Though they probably represent mixtures which are of service for some specific condition, yet they are often unnecessarily complicated. Because they shed little light on the properties of silicates only a few are cited.[42-49]

Automobile Frames. Silicate films are applied to wooden members of automobile frames to permit the use of higher temperatures in ovens where finishes are baked on the metal parts. Temperatures up to 230°C. (450°F.) are used, and the silicate-coated wood is uninjured on 40 minute exposure.

Prevention of Oxidation on Sheet Iron and Coating of Metal Ware. Similar treatment of sheet iron to prevent oxidation at temperatures sufficient to cause it without the coating have proved effective. They have also been found useful for coating metal ware previous to

[42] Wortelman, G. A., U. S. Pat. 1,397,028 (Nov. 15, 1921).
[43] Welles, C. E., U. S. Pat. 1,436,618 (Nov. 21, 1922).
[44] Vivas, F. S., U. S. Pat. 1,369,857 (March 1, 1921).
[45] Iversen, M. M., Nor. Pat. 33,924 (Jan. 30, 1922).
[46] Locke, J. A., Brit. Pat. 160,801 (March 24, 1921).
[47] Ferrell, J. L., Ger. Pat. 162,043 (1905).
[48] Felix, Charles R., U. S. Pat. 1,643,116 (Sept. 20, 1927).
[49] Young, Ira Benjamin, and Harry R. Haywood, U. S. Pat. 1,505,519 (Aug. 19, 1924).

the enameling process, as the surface is thus more easily kept clean and free from rust.[50]

Soluble silicates have been used to moisten asbestos or cellulose fibers applied to metal surfaces with phenol-aldehyde condensation products.[51]

Miscellaneous Uses for Silicate Films.

Half Tone Cuts. An interesting use of a silicate film is involved in a method for rapid production of overlays or impressions of half tone cuts for printing. A mixture of rosin and emery powder is dusted on a freshly inked proof and set by heat. The paper is then dipped in a silicate solution, one part Na_2O, $3.3SiO_2$, 1.4 specific gravity, and 3 parts water by measure. This is quickly dried and it imparts enough rigidity to withstand the operation of printing.[52]

Silicate-Coated Walls. The outside wooden walls of certain tobacco warehouses are periodically painted with silicate to reduce the escape of moisture.

Silicate has been successfully used to coat old walls which were so permeated with soot and grease that plaster could not be applied without staining through. A silicate coating prevented the staining and gave a satisfactory base for the plaster. Dilute silicate solutions may be applied to the surface of new plastered walls to facilitate the adherence of paint.* Treatment of metallic surfaces to help the adherence of magnesium oxychloride cements has been accomplished with or without admixture of clay or other minerals.[53]

Sizing on Jute Sacks. Na_2O, $3.3SiO_2$, specific gravity 1.4, diluted with 9 measures of water has a sizing effect on jute sacks used as containers for acid calcium phosphate or fertilizer mixtures which contain free acid. The acid causes the rapid weakening of the fiber, being most troublesome in hot weather. The silicate delays but does not completely prevent this action. Calcium acetate and paraffin are also used. The latter is effective in cool weather but not in the summer temperatures encountered in the Southern States where most of the acid phosphate is made. The silicate treatment adds nearly 50 per cent to the weight of a sack with a 9 to 1 dilution and somewhat more with a ratio 6 to 1 between the original solution and water.

Tree Wounds. Silicate films have also been found useful as a dressing for pruning-wounds of trees. They serve the double purpose

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* Cf. page 271.

[50] Nicksch, K., Z. ger. kohleus Ind. (1919) ; Rev. chim. ind., **28**, 267 (1919) ; C. A., **14**, 3802.

[51] Wirth, J. K., Brit. Pat. 188,187 (Oct. 22, 1921).

[52] St. Paul, Johns, U. S. Pat. 1,441,283 (Jan. 9, 1923).

[53] Davies, J., and W. H. Miles, Brit. Pat. 186,231 (Aug. 24, 1921).

of reducing the loss of sap and of keeping out the spores from which spring the fungus growths which cause destruction of the wood.[54]

Two pruning wounds are shown in Figure 135. They were made at the same time. The upper one was painted with a viscous solution of $Na_2O, 3.3SiO_2$, and healed rapidly and clean while the lower one became a host to fungi which would ultimately cause deep destruction. The

Fig. 134.—A Pruning Wound Showing Entrance of Rot. (Courtesy of Ohio State Agricultural Experiment Station).

Fig. 135.—Healing of Pruning Wound. Infection of Untreated Wound by Fungus (Courtesy of Ohio State Agricultural Experiment Station).

coating is not necessarily heavy enough to give a glassy film, but the treated surface should become dry and hard. It is probable that the best results could be had from the most silicious silicate, which would not only dry faster, but be less likely to be washed away before gelation due to the combined action of sap and carbon dioxide. This action is partly mechanical, but the alkalinity of the silicate is useful against organisms which thrive in an acid medium.

Stainproofing Lumber. Moist hot climates give rise to blue stain, a fungus growth which readily attacks and disfigures freshly cut lumber. It requires an acid medium in which to grow and the lumber can be protected by passing through an alkaline bath. Silicates have

[54] Young, W. T., *Ohio Agri. Exp. Station Bull.*, **8**, 13-17 (1923).

the advantage over other alkaline materials of remaining close to the surface and are at the same time less soluble. A concentration of 1.07 specific gravity is sufficient for $Na_2O, 3.3SiO_2$.

Parting Films. In spite of their adhesive character and the fact that they can under some conditions be laid on rubber surfaces, silicate solutions are useful for making parting films between iron molds and plastic rubber masses. Particularly in the making of hard rubber jars and the like, a silicate film on the mold gives a smooth surface and a ready separation. On account of the need of removing this film it is best to use $Na_2O, 2.9SiO_2$ or even $Na_2O, 2SiO_2$, which can be readily cleaned away with hot water. The objection to too great an alkalinity is slowness of set.

Films of more silicious silicates on paper serve as separators for light rubber goods before vulcanizing.

Coatings on Metal.

Zinc Loss. Remelting of finely divided metal scrap such as turnings is, if the alloys contain zinc, subject to a loss by the oxidation of that metal. This may be reduced by dipping the turnings into a silicate solution of suitable strength to coat each particle with a thin film. There is some latitude in the selection of a silicate for this purpose, but good results appear to be obtainable with $Na_2O, 4SiO_2$ at about 1.1 specific gravity.

Induration of Defective Castings. Induration of porous metals or defective parts of castings has long been practiced and appears to yield satisfactory results for steam engine cylinders and other pressure vessels made by casting, provided of course that the openings are not too large. The most effective method of application is to place the castings in vessels from which the air should be exhausted, then to immerse them in silicate and finally to apply pressure. This has been successfully done with light metal alloys for use in equipment of air craft. Another method is to plug up the casting so that the solution shall be applied from one side only. $Na_2O, 3.3SiO_2$ 1.05 to 1.10 specific gravity or 3 to 5 measures of water to one of 1.39 specific gravity is used according to the degree of porosity and the size of the casting. The solutions are used hot, 70° to 90°C., and pressures up to 4.93 kilograms per square centimeter (70 pounds per square inch) are applied and maintained until the solution does not sweat through, or for 10 to 20 minutes.[55]

[55] Air Service U. S. Army Specifications No. 20,002-A (Sept. 25, 1921).

In some cases it is sufficient to soak the casting in the warm silicate. After the treatment the castings are washed, dried, and subjected to double the pressure required of them in service, or not less than 0.703 kilogram per square centimeter (10 pounds per square inch). The testing liquid is kerosene. The process is applicable only to castings with a degree of porosity which results in but slow seepage of liquid. It cannot be expected to close openings large enough to allow spurting of liquid under pressure. Aluminum castings are easier to deal with than a metal which does not react at all with the silicate, but numerous unpublished confirmations of the fact that it serves well on iron are available.

Silicates have been used as incidental reagents in making metallic coatings which are glossy because of the presence of a colloidal compound which prevents the liberation of hydrogen at the cathode.[56]

SILICATE PAINTS.

NATURE OF PAINT.

Requirements of the Paint Film. Paints are systems in which a more or less viscous liquid causes the suspension of finely divided matter insoluble in the vehicle. They must harden to form films fit for decorating or for protective service on widely varying surfaces. Silicate films alone have been described; the introduction of pigment increases their range to provide color, opacity, or light-diffusing power and added resistance to chemical influences. Silicate stains, i.e., soluble colors dissolved in silicate solutions, have been proposed but not widely used.[57]

Factors Governing Consistency of Paint. The working properties of a paint, its behavior under brush, spray, or dipping, have much to do with the ability to make uniform films of appropriate thickness. Paint consistency depends upon yield value and mobility, which are governed by viscosity of vehicle, ratio between vehicle and pigment, the force of flocculation in vehicle and pigment, and particle size of the pigment.[58] All these can be adjusted in a paint with a vehicle of soluble silicate. It is therefore possible to make a paint with the physical characteristics desired for spreading, and the limitations of its use will be found in the character of the finished film or in some cases the keeping quality of the mixture.

Color of Vehicle. Most liquids suitable for paint vehicles affect the color of the film. Silicate solutions, being colorless, have a great advantage over oils for coatings of maximum reflecting power. It is

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[56] Classen, Alexander, U. S. Pat. 1,491,381 (April 22, 1924).
[57] Puscher, *Chem. Zentr.*, 277 (1870) ; *Chem. Zentr.*, **42**, 448 (1871).
[58] Green, Henry, *Ind. Eng. Chem.*, **15**, 122-126 (1923).

believed that the whitest paint known can be made from some of the modern types of lithopone in silicate vehicles. Such paints are used to make light-diffusing surfaces in apparatus required to produce light of known quality for colorimetric and similar work. As a flat white is required, $Na_2O, 3.3SiO_2$ is used at about 1.16 specific gravity (20° Baumé).

Suitable Pigments.

It was early observed that some pigment materials such as white lead react and cause silicate solutions to gel. This may in some cases be offset by grinding the pigment previously in a silicate solution and thus rendering the surface of the particles relatively inactive. Creuzburg [59] proposed alternate layers of silicate and of pigment in a vehicle with which it does not react, but this is too laborious for modern uses. The better means is to choose coloring materials compatible with the silicate, as there are enough of them to give a wide range of tints. Clays, silica, lithopone, whiting, barytes, and, under some conditions, zinc oxide are available for white. Ultramarine or smalt [60] give good blues. Chromium oxide gives the most satisfactory green, though lead chromate ground in silicate and mixed with ultramarine may be used. Ochers and umbers make good yellows and browns. Cinnabar or iron oxides free from lime serve for reds. Grease-free carbon blacks can be used. In addition to these, there are numerous alkali-resisting lakes available.[61] Of metallic pigments, aluminum, either pure or alloyed to give yellow colors, copper, zinc, and lead can be mixed with the most silicious solutions.

Silicate Vehicles.

Specific Gravity of Silicate. Any silicate solution with three or more molecules of silica may serve as a vehicle for paint. The concentration chosen will determine the degree of gloss and to some extent the tendency to crack. For permanent exposures for decorative purposes the specific gravity should not be more than 1.19 (24° Baumé). The vehicle prepared by neutralizing a part of a silicate solution with acid and preventing gelation by mixing in a further quantity of silicate yields a film which is insoluble in water a few minutes after spreading.[62] Other silicates without this treatment become insoluble in course

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[59] *Dingler's polytech. J.,* 144, 292-295 (1857) ; Abst. in *Chem. Zentr.,* **28,** 428-430 (1857).

[60] Fisher, Harry C., U. S. Pat. 1,631,628 (June 7, 1927).

[61] Wagner, H. von, *Chem. Zentr.,* **47,** 128 (1876).

[62] Carter, J. D., and J. G. Vail, U. S. Pat. 1,129,320 (Feb. 23, 1915).

of time by taking up carbon dioxide and forming a binder of gelatinous silica similar to the first. It is not always possible to await this slow action, however, lest the soluble silicate be washed away. The picture shows the comparative weathering of a silicate paint, 1, and 3 commercial casein paints.

Fig. 136.—Comparative Weathering of Silicate Paint.

Britton [63] proposes a paint vehicle made by peptizing gelatinous silicic acid in a silicate solution with the same object. Alkaline bicarbonates heated with silicate solutions have also been proposed.[64]

Kind of Silicate. Potassium silicates show less tendency toward efflorescence than the corresponding sodium silicates; and the latter of low alkalinity, as $Na_2O, 4.2SiO_2$, less than the ordinary grades of commerce; but all are likely to show some white "bloom" against the background of a dark pigment. Carbonate efflorescence is easily removed by washing.

Light Diffusion.

Decorative Lighting Effects. A method of avoiding efflorescence and adding resistance to water in a silicate paint used as a light diffuser in place of frosting on electric lamps is to coat the dry silicate-painted surface with dammar varnish.[65-68] A very light coating made from a varnish much reduced with turpentine is sufficient.

Opal glass is simulated by using zinc oxide, French chalk and hydrated magnesium silicates. These are ground in a ball mill with water and little or no silicate of soda, and the principal amount of silicate is put in near the time the paint is to be used. The formulas are the following:

[63] U. S. Pat. 1,477,938 (Dec. 18, 1923); Brit. Pat. 191,426 (Sept. 7, 1921).
[64] Gallenkamp, W., Ger. Pat. 294,330 (April 1, 1916).
[65] French Thomson-Houston Co., Fr. Pat. 555,691 (March 28, 1923).
[66] British Thomson-Houston Co., Brit. Pat. 113,769; Brit. Pat. 150,598 (Jan. 8, 1920).
[67] Luckiesh, M., U. S. Pat. 1,464,101 (Aug. 7, 1923).
[68] See also Dixson, James Q., U. S. Pat. 587,799 (Aug. 10, 1897).

White		Yellow	
French chalk	15	French chalk	26
Zinc oxide	15	Burnt sienna	13
Water	25	Water	24
Sodium silicate sp. gr. 1.375,		Silicate	37
presumably $Na_2O, 3.3SiO_2$ ..	45		

This is put on with brush or spray. The glass may have been roughened by sand blasting, but this is not essential. The paint hardens in a few minutes, when the varnish may be applied by brush or dip. Lamps thus treated give a good diffused light with less loss than indirect methods of illumination. A further step consists of omitting the varnish coating and causing the dried silicate film to become insoluble by dipping it in a bath of a reacting salt or acid. Zinc chloride, aluminum sulfate, other soluble salts of zinc, tin, and alkaline earth metals, ammonium fluoride, ammonium chloride, sodium chloride and sulfuric acid have been used. After treatment with the precipitant the coating may be washed, after which it is free from efflorescence. For lamp coating, the oxides of magnesium, aluminum, zinc, and tin have been used as opacifiers.[69, 70]

These coatings are cheap, durable, and well adapted to give decorative lighting effects.

Another step has been the application of silicate paints to the inside of the lamp bulbs, which, contrary to expectation, have shown a satisfactory life in spite of the impossibility of completely dehydrating the silicate film. It has been found that good adherence of a sprayed film to the glass can be had on surfaces which are scrupulously clean. The addition of a small amount of ammonia to the paint reduces surface tension and makes adherence easier.[71]

Screens for Lanterns and Motion Pictures. A light-diffusing silicate paint adapted for screens for projecting lanterns is made from:

> 100 parts $Na_2O, 3.3SiO_2$, 1.38 specific gravity
> 15-20 parts rice starch
> 200-300 parts water

This is applied to a glass plate, which then serves as well as ground glass. It can also be used for focusing glass for cameras, etc.[72]

The same object has been sought in a motion picture screen of glass coated with zinc sulfide in a silicate vehicle. Calcium sulfate is also specified, but its quick reaction with the less alkaline silicates makes it

[69] Whitmore, James Bryant, U. S. Pat. 1,581,766 (April 20, 1927).
[70] British Thomson-Houston Co., Brit. Pats. 185,910 (July 18, 1921); 196,843 (June 21, 1922).
[71] Osgood, Samuel W., U. S. Pat. 1,169,506 (Jan. 25, 1916).
[72] Eberlin, L. W., and S. E. Sheppard, U. S. Pat. 1,421,924 (July 4, 1922).

impracticable to obtain a smooth coating.[73] $Na_2O,2SiO_2$ might serve but is not specified.

Coatings on Wood.

Effect of Diluting the Silicate.   Sprayed silicate paints on brick, stone, or concrete surfaces last for years, but on wood, which is subject to changes of moisture and consequent expansion and contraction, they tend to crack. A paint made from two parts of whiting and one of lithopone with substantially an equal weight of the special silicate, 1.17 specific gravity, containing metastable silica resisted exterior exposure on a brick wall in Philadelphia for five years. The same paint on interior brick and concrete remains intact at this writing, eight years after it was spread.*   If checking of silicate coatings on wood be avoided by diluting the silicate, reducing it relative to the pigment, the binding action will not be sufficient, and chalky films will be formed which do not resist even mild abrasion.
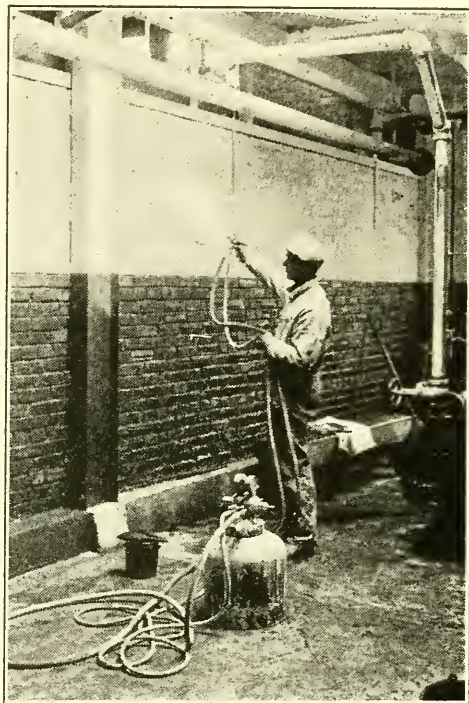
Fig. 137.—Spraying a Silicate Paint.

Addition of Rubber Latex. An improvement consists in grinding the pigment in the silicate and then adding rubber latex stabilized with ammonia.[74, 75, 76]   If the latex were put in during grinding, it would coagulate. Delayed addition of the latex improves the brushing consistency of the paint and softens the film enough to permit its use on wooden surfaces. The lithopone is flocculated by the concentration of silicate needed for binder though the same silicate at lower concentration is an effective means of deflocculating.

The limiting proportions of latex are 10 to 20 per cent by weight of the vehicle. It is desirable to add 0.1 to 1 per cent of borax or

[73] Gilpin, R., Brit. Pat. 166,015 (May 19, 1920).
* *Cf.* page 264.
[74] Drefahl, Louis, and Edward Taylor, U. S. Pat. 1,486,077 (March 4, 1924).
[75] Teague, M. C., U. S. Pat. 1,550,466 (Aug. 18, 1925).
[76] American Rubber Company, Brit. Pat. 235,888 (June 18, 1924); *C. A.,* **20,** 1004.

sodium benzoate to the latex to prevent fermentation of its protein content. A typical formula is:

Pigment 50 per cent $\begin{cases} 99.8\% \text{ lithopone.} \\ 0.2\% \text{ borax.} \end{cases}$

Vehicle 50 per cent $\begin{cases} 90.0\% \text{ 22}°\text{Baumé Na}_2\text{O, 3.3SiO}_2 \text{ treated by} \\ \quad\quad \text{Carter process.} \\ 10.0\% \text{ rubber latex stabilized with ammonia.} \end{cases}$

This mixture kept sealed in a can was in good condition after six months. It may be applied to damp surfaces. It can be thinned with a little $Na_2O,4SiO_2$, 34° Baumé, if necessary. It works with either brush or spray.

The extent to which the addition of materials which do not dissolve in the silicate are able to modify the films is related to the manner and degree of dispersion. Films made from emulsions exhibit primarily the properties of the continuous phase. When this is a silicate solution the film is therefore affected by water and never exhibits the degree of flexibility which might be implied from its rubber or oil content. Emulsions in which silicate solutions were dispersed in oils would correspondingly lack some of the advantages peculiar to the silicate.

MISCELLANEOUS USES.

Protective Coating for Whitewash. A series of tests by Fink [77] indicated that silicates may make good protective coatings for whitewash and be of service in connection with casein paints. He used the special solution containing metastable silica, which is probably not the best for use with casein. Arthur, Mitchener, and Withrow [78] recommend the use of silicate of soda in mixtures designed to improve upon ordinary whitewash as a coating for brickwork, more or less heated, as it is in many industrial processes.

Stereochromic Painting. [79-85] The older literature of the soluble

[77] *J. Ind. Eng. Chem.,* 14, 503-511 (1922).
[78] Arthur, Edwin P., W. B. Mitchener, and James R. Withrow, *Ind. Eng. Chem.,* 19, No. 5, 591 (1927).
[79] Rivington, *J. Soc. Arts,* No. 1630, Feb. 15, 1884.
[80] *Encyclopedia Britannica,* 11th ed., 20, 488-489.
[81] Kleim, A., "Mineralmalerei," Wien, 1881.
[82] Bersch, Josef, "Die Malerfarben und Malmittel," Wien: Hartleben's chemisch-technische Bibliothek, 1905, p. 28-37, 180-184.
[83] Feichtinger, G., *Poly. J.,* 210, ser. 5, 10, 440-444 (1873). Same, condensed, *Chem. Zentr.,* 45, ser. 3, 5, 74-75 (1874). Same, abstract, *Neueste Erfindungen und Erfahrung,* 1, 60-61 (1875). Same, abstract translation, *Bull. soc. chim.,* 26, n.s. 21, 280-282 (1874).
[84] "Peinture murale," *Le Montieur scientifique,* 6, 800 (1864).
[85] Pettenkofer, Max, *Poly. J.,* 113, 217-225 (1894).

silicates lays great stress on stereochromic painting, a form of fresco painting devised by von Fuchs and used by artists more or less continuously since. It consists in preparing a porous surface of plaster upon which a picture is wrought with pigments in any aqueous medium. These are then fixed by spraying repeatedly with a hot dilute solution of silicate until the plaster is saturated. Potassium silicate is always specified on account of its comparative freedom from efflorescence; but if the final step is to apply a solution of ammonium carbonate as directed by Cremer,[86] and washing with distilled water to remove the potassium carbonate formed, it seems that a sodium silicate would be satisfactory. Numerous notable mural paintings have been done by this process; success depends upon the preparation of a uniform porous ground and the use of colors specially prepared for the process. They must not only be resistant to alkali, but they must be mixed with gum arabic or other colloids such as silicates, which modify and control their behavior. In some cases it is advantageous to use colors ground in silicate solutions. The finished work after drying is treated with a solution of paraffin in benzol, which has the effect of brightening the colors and keeping the water away from them for a time.

Metallic Paints. Paints with a silicate vehicle and metallic pigment are serviceable on hot surfaces where they reduce radiation losses and withstand for a long time the effect of temperatures up to red heat.[87] Aluminum powder reacts sufficiently with silicates, even $Na_2O, 4.2SiO_2$, to make it unsafe to store in tight cans which may be exposed to enough heat to cause the can to burst from the pressure of liberated hydrogen. When mixed immediately before use, it makes a pleasing and highly durable coating for furnace doors, stoves, and other hot apparatus in which heat conservation is an object and where a paint containing organic material would readily burn off. Edwards[88] gives the following precautions:

"However, not all brands of sodium silicate have been found to be equally effective. If there is excessive frothing when the aluminum bronze powder is mixed with the solution, this is an indication that it is not, perhaps, the best grade which can be secured for this purpose, although, unless the frothing is excessive, it need not necessarily interfere with the successful application of the paint. It is found that dilut-

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[86] "Beiträge zur technik der Monumental Malverfahren," Düsseldorf, **1895.**
[87] Coblentz, W. W., *Architecture and Building*, **55**, 93 (1923). Coblentz, W. W., and C. W. Hughes, *Bur. Standards Tech. Paper* No. 254, 171-187.
[88] Edwards, Junius D., "A Treatise on the Physical Properties of Aluminum Paint and Its Uses in Industry," Pittsburgh: Aluminum Company of America, **1924.**

ing the silicate to a density of 22° to 28° Baumé gives a vehicle of the proper consistency. . . . The surface to which the paint is to be applied should be sufficiently rough, however, to assure the proper bonding of the paint. In case of doubt, the adherence can be tested by preliminary experiment. It is essentially, however, an interior paint, although moderate success has been had with the application of it to exterior cement work. In the latter case, the sodium silicate seems to combine with and become insolubilized by the concrete surface, with the result that very good adherence is usually secured. In some cases, where rain destroyed the adherence of the paint film, the difficulty proved to be due either to the vehicle or to the fact that the cement work was new. Such a vehicle only costs about 25 cents per gallon, so that it makes a very economical paint for uses where its properties are satisfactory." It is important to have the surfaces free of grease or oil. The presence of a small amount of soap in the paint appears to reduce the surface tension and facilitate spreading.[89]

One and a third to one and a half pounds of aluminum powder per U. S. gallon of 22° Baumé Na_2O, $3.9SiO_2$ give a paint which works well on concrete and brick interiors and on exterior concrete which has been sufficiently aged. These should be mixed within a few hours of use to avoid frothing, as bubbles of hydrogen make uniform spreading difficult. Only silicates high in silica are suitable for this use.

Decorative Coatings on Wallboard. Gold or aluminum bronze paints make decorative and permanent coatings on wall board or wood surfaces. If these surfaces are very porous it is best to give them a sizing coat of silicate. The coatings do not entirely prevent rusting of iron.

Pulley Dressing. Silicate paints containing abrasive material have been used to increase the traction of wooden and steel pulleys, which are thus enabled to take better hold of belts for the transmission of power.[90]

Printers' Ink. Small additions of any silicate solution thoroughly mixed into printers' ink are a convenient means of increasing its viscosity. Many a print shop keeps a can of silicate handy against the time when the ink works a little too thin on the presses. The more silicious grades are preferable for this purpose. Similar results are to be had in oil paints, which develop a better pull on the brush when a little silicate is ground in with the pigment. This should never be done in a paint for exterior use, as it lowers the resistance of the film to

[89] Seideman, Leon, U. S. Pat. 1,452,445 (April 17, 1923).
[90] Benford, David M., U. S. Pat. 1,383,692 (July 5, 1921).

water. Amounts of the order of one per cent give a marked change in flow, partly due to saponification and partly to the emulsifying action of the silicate.[91]

Coating Heat Exchangers. Imison and Russell [92] describe the use of a silicate paint to protect iron heat interchangers used for the oxidation of ammonia. This consisted of 73-75 per cent barium sulfate in a finely divided condition and 10 per cent $Na_2O,4SiO_2$. It was reduced to a painting consistency with water and applied to the iron surface which had been heated to 200°C. This process was several times repeated and resulted in a coating which would stand a full red heat and long service without corrosion of the metal. It was found very difficult to make satisfactory coatings on large apparatus.[93]

Refractory Paints. Other silicate paints have been proposed to impart refractory properties to bricks [94] but have found a rather limited use. For high temperatures something more than a film is needed. A mixture of 75 per cent carborundum and 25 per cent silicate solution may reduce chemical attack at the surface but must be supported on a foundation capable of resisting the temperatures encountered in furnaces or gas retorts.[95]

Paints made from silicate solutions and clay form glazes on furnace linings and glass pots which reduce the penetration of gas or fluxing liquids.

Silicate solutions have been used to toughen the coating of electron-emitting electrodes in thermionic valves.[96]

Electrodes for Welding. Wire electrodes for arc welding are coated with silicate paints containing asbestos to prevent oxidation at the high temperature applied for a short time in this process.[97-99]

Pottery Glazes. Ceramic colors painted upon surfaces to be decorated with the aid of a silicate binder which sets in the air and permits of easy handling have been found convenient and economical,[100, 101] and zinc silicate glazes applied in this manner have yielded some of the most beautiful crystalline effects. Kraner [102] found that a step in the prepara-

[91] Bourcet, P., and H. Regnault, Ger. Pat. 415,062; *Zellstoff u. Papier,* **5,** 267 (July, 1925).
[92] *J. Soc. Chem. Ind.,* **41,** 37-45T (1922).
[93] Imison, C. S., personal communication.
[94] Stowell, E. R., U. S. Pat. 774,003 (Nov. 1, 1904).
[95] *Chem. & Met. Eng.,* **24,** 1070 (1921).
[96] Krogh, A. T., Brit. Pat. 255,830 (July 23, 1925).
[97] King, Jesse C., U. S. Pat. 1,312,256 (Aug. 5, 1919).
[98] Boorne, William Hanson, Brit. Pat. 185,580 (Sept. 14, 1922).
[99] Holslag, Claude J., U. S. Pat. 1,451,392 (April 10, 1923).
[100] Keram. *Rundschau,* **28,** 239 (1920).
[101] Fenaroli, Pietro, U. S. Pat. 1,164,710 (Dec. 21, 1915).
[102] *J. Ceram. Soc.,* **7,** 868 (1924).

tion of these glazes could be omitted by using a silicate solution as binder for the glaze materials and calculating the soda and silica of the silicate as part of the final composition. In this way the alternative of frit, weakly attached with an organic binder which had to be burned out at a low temperature prior to the final firing, was avoided and decorative effects of rare beauty were obtained. Zinc silicate crystals

Fig. 138.—Crystalline Zinc Silicate Glaze.

are able to absorb certain coloring materials, such as the oxides of cobalt, manganese, copper, uranium, nickel, and iron in such a way that bright colored crystal masses appear upon a background of contrasting color. It is not possible to present this adequately in monochrome, but the author possesses two vases similar to those shown in the cut. Their surfaces are strewn with delicate blue crystal tracery on a background of brownish buff, most pleasing to the eye. Many color combinations are possible.

A silicate solution of 47° Baumé (13.7% Na_2O, 32.9% SiO_2, and 53.4% H_2O) is not appreciably absorbed by whiteware or faience biscuit with as much as 10 per cent water absorption. This may be used

with a willemite or zinc silicate glaze without affecting its fusion properties. The silicate and glaze ingredients are mixed to a smooth consistency and applied to the surface of the ware by dipping or brushing; the coating is then allowed to dry to the similitude of a thick varnish. The pieces may then be handled without danger of injury. The water is not completely removed on air drying and some intumescence is noted in the early stages of firing, but the coat soon settles back without loss of material from the surface. The batch weight used was the following:

	Per Cent
Sodium silicate	49.69
Flint	19.46
Zinc oxide (ZnO)	17.95
Titanium oxide (TiO₂)	7.94
Water	4.96
	100.00

Coloring materials were added as required, but always in small amounts.

Optimum conditions for firing consisted in raising the temperature uniformly to 1200°C. in 10 to 13 hours and cooling to 900°C. between the 16th and 17th hours.

The success attained with this process suggests that a silicate vehicle may be of use for sundry other ceramic uses where an impermeable surface is required with or without decorative quality.

Dry Paint Mixtures.

Since hydrous silicates of several ratios are available in powder form and these are much more soluble than the anhydrous powders of like ratio, it appears logical to make some of the paint mixtures in dry form, requiring only the addition of water. This has been done. They require more care than the wet preparations. If cold water is to be used, it is generally necessary to use more silicate to allow for something less than complete solution. The mixtures should be stored in air-tight metal containers to prevent the decomposition of silicate by carbon dioxide. The danger of separation of the dry silicate from other ingredients must be guarded against. If casein is present, the most favorable sequence of reaction is not possible. Some silicate may be decomposed by lime before it performs any useful function. Nevertheless there are many silicate paints which, with a little study, could be prepared dry with a gain in convenience to the user; and there are several known factors to supplement the method of trial and error.

Patent Literature.

The patent literature of silicate coatings is voluminous. Ingredients such as casein, glucose, glue, glycerin, pigments, and fibrous materials can be mixed with silicate solutions in innumerable permutations. The patents cited are typical.[103-119]

Analysis.

The analysis of silicate paints is difficult unless the ratio between Na_2O and SiO_2 in the original vehicle is known. If the silica content of the pigment is not known, it is difficult to assign the proper source to all the silica found. As in the case of cements, reactions take place which may render ultimate analyses misleading.[120]

Paper Sizing.

Silicate Sizing.

Relation between Soluble Silicates and Rosin. The process of sizing paper consists in depositing upon or among the fibers which form the sheet colloidal substances so chosen as to modify the finished product to fit it for specific uses. Rosin is the material mostly used, and its primary contribution is to impart a resistance to water. It does not give to paper all the desirable qualities, and as forest reserves are depleted its cost increases. These two considerations have led to the use of several other colloids which serve in some instances by themselves and in other cases in an accessory capacity.

The soluble silicates fall into this group. To understand their place in the industry it is necessary to have clearly in mind their relation to

[103] Philipp, Ferdinand, U. S. Pat. 300,890 (June 24, 1884).
[104] Fewins, Frank N., U. S. Pat. 443,361 (Dec. 23, 1890).
[105] Bibikon, N. A., U. S. Pat. 421,229 (Feb. 11, 1890).
[106] McLennon, Charles J., U. S. Pat. 872,960 (Dec. 3, 1907).
[107] Connolly, J. P., Can. Pat. 177,506 (June 5, 1917).
[108] Sharp, Robert, U. S. Pat. 1,309,782 (July 15, 1919).
[109] Hutchison, A., Brit. Pat. 153,081 (July 28, 1919).
[110] Isaacs, M. R., Brit. Pat. 150,551 (Oct. 8, 1919).
[111] Morrison, Freeland, U. S. Pat. 1,365,716 (Jan. 18, 1921).
[112] Mees, E. F., U. S. Pat. 1,396,970 (Nov. 15, 1921).
[113] Walsh, M. J., U. S. Pat. 1,415,282 (May 9, 1922).
[114] Keedwell, C. A., U. S. Pat. 1,476,016 (Dec. 4, 1923).
[115] Sulzberger, N., U. S. Pat. 1,518,944 (Dec. 9, 1924).
[116] Plönnis, Rudolf, U. S. Pat. 1,487,471 (March 18, 1924).
[117] Blombery, George Frederick, U. S. Pat. 1,582,117 (April 27, 1926).
[118] Gaudry, Tanciede, U. S. Pat. 1,604,904 (Oct. 26, 1926).
[119] Bristow, John J. Rucker, U. S. Pat. 1,635,110 (July 5, 1927).
[120] Coffignier, C., *Rev. chim. ind.*, **28**, 299-301 (1919).

the process of sizing with rosin.[121, 122] Both are alkaline colloidal materials, for rosin is always dispersed by making a soap which contains more or less free rosin. In their alkaline condition they are not retained by cellulose fiber and would be lost in the process of making paper unless a precipitant were used. Various salts and acids have been tried, but the one in almost universal use is aluminum sulfate, known as papermaker's alum. The theory of rosin sizing has not been set forth in such a way as to be completely satisfying, but it is evident that both aluminum hydroxide and colloidal rosin play a part in giving the paper the ability to resist the penetration of water or aqueous inks. It has been assumed that rosin sizing and soluble silicates are incompatible.[123] This is an error. It is necessary to add a sufficient amount of alum to precipitate both silicate and rosin when they are used together, just as they must each be precipitated when they are used separately.[124] Pulp which has been treated with rosin size and just enough alum will not be properly sized if made alkaline with silicate. When the silicate is precipitated with alum both are in condition to be retained and to affect the finished paper.

Characteristics of Silicate Sizing. Though the silicate precipitate does not impart waterproof qualities to paper, except as it assists in retaining rosin or increases the hydration of the fiber, it hardens it and makes a smoother surface. It increases strength; it reduces the tendency of cut sheets to curl, improves color by helping to retain pigments, and likewise helps to save small fibers which would otherwise have to be recovered from the waste waters, if saved at all.[125] It makes possible a good printing paper which is not susceptible to discoloration, as rosin-sized papers are, on exposure to light. Mineral sizing is mostly used in connection with and supplementary to rosin sizing. In addition there are sundry operating advantages which will be mentioned later.

The extent to which silicate sizing is useful in paper was pointed out by Klemm,[126] who distinguished between the need for paper surfaces to resist water and those which should have good printing quality without necessarily passing a water test.

Effect of Alum on Rosin and Silicate. When rosin size is diluted to the concentrations encountered in paper sizing, small additions of

[121] *Papeterie,* **43**, 1058-1066 (1921).
[122] Vail, J. G., *Chem. & Met. Eng.,* **25**, 823-824 (1921) ; Abs. *J. Soc. Chem. Ind.,* **40**, 884a ; *C. A.,* **16**, 492 ; *Ind. Digest,* **1**, 337 (1921) ; *Paper Trade J.,* **73**, No. 17, 32-34 (1921) ; **74**, No. 1, 49 ; *Paper,* **29**, No. 6, 19-20 (1921).
[123] Bert, Henry, *Fibre Containers,* **6**, No. 2, 14 (1921).
[124] Vail, J. G., *Fibre Containers,* **6**, No. 3, 16 (1921).
[125] Stericker, Wm., *Paper,* **33**, No. 7, 8 (1923).
[126] *Wochbl. Papierfabr.,* **38**, 1983 (1907) ; **40**, 1007 (1909) ; *C. A.,* **1**, 2490.

alum cause precipitation which increases with increase of precipitant until the separation is nearly complete. In contrast to this, silicate solutions become turbid. Their opalescence increases as alum is added, but separation begins only if almost all the alum needed has been put in. It thus appears that while a slight under-dosage of alum may cause minor losses of rosin size it may result in the entire loss of silicate. Silicate flocculation is similar in appearance to that of aluminum hydroxide. The flocs increase in size and slowly settle to the bottom of the containing vessel when alum has been added to about pH 5.

Nature of the Precipitate with Alum. The composition of the precipitate varies with the alkali-silica ratio of the silicate. This may be due only to the fact that more alum is required to neutralize the larger amounts of soda, but the precipitate seems to be something more than a mixture of aluminum hydroxide and silica. A hot solution of acid potassium sulfate has little solvent effect on freshly precipitated silica but dissolves aluminum hydroxide. The floc which results from precipitating silicate with alum is soluble in hot solutions of acid sodium or potassium sulfate. This suggests but does not prove a combination. There may be some aluminum silicate formed.[127] The floc always carries sodium out of solution, presumably adsorbed, as its amount does not vary greatly with changes in the composition of the precipitate. Precipitation of the silica is more nearly complete in the more concentrated solutions and it is believed that this is also true of the solutions of lower relative alkalinity, though accurate data on this point are lacking. Certainly the silica in $Na_2O,4SiO_2$ is less stable in solution than that in $Na_2O,2SiO_2$.

TABLE 86. *Precipitation of Silicate by Alum.*

Solutions Used

Silicate Composition	Concentration Per Cent	Amount of Silicate Solution, cc.	Amt. Alum .00169 Al_2O_3 per cc.
$Na_2O, 3.86SiO_2$	1.56	51	65
$Na_2O, 3.3SiO_2$	0.13	401	47
$Na_2O, 2.45SiO_2$	1.25	36	51

Precipitate

Silicate Composition	Per Cent SiO_2 in Ppt. Dry Basis	Per Cent Al_2O_3	Per Cent Na_2O + Undetermined	Per Cent Total SiO_2 Ppt.	Per Cent of Total Al_2O_3 Ppt.
$Na_2O, 3.86SiO_2$	81.1	14.5	4.5	89.4	83.3
$Na_2O, 3.3SiO_2$	68.0	36.3	5.4	43.9	80.5
$Na_2O, 2.45SiO_2$	73.6	21.7	4.7	83.3	100.0

[127] Carter, J. D., unpublished records of the Philadelphia Quartz Company.

Blasweiler found that the yields from metasilicate in the process used above were very low and concluded on this account as well as because of the greater cost of the silicate that this is uneconomical compared with $Na_2O,3SiO_2$.

Experience with production on a large scale points to the desirability of using the highest ratio of silica attainable. The limit in this direction is reached not because there is any silicate solution too silicious for paper sizing, but because solutions with more silica than $Na_2O,4SiO_2$ are too costly (cf. Chapter VI). $Na_2O, 3.3SiO_2$ can be produced at lower cost than any soluble silicate with less base because the solubility of all more silicious products is so much slower that they seriously reduce the output of manufacturing equipment.

Blasweiler [128, 129] did not find that more than 72 per cent of the silica used was retained in the finished paper when the precipitation of $Na_2O,$-$3.3SiO_2$ was conducted in the presence of pulp. As sodium chloride or any other electrolyte except the alkaline hydroxides will tend to reduce the stability of silica sols, he considered the possibility of increasing the yield by adding sodium chloride to salt out the silica, but found it uneconomical.

The precipitate always contains water. Example 2 of the foregoing table contained 18.4 per cent of water which could not be removed at 100°C. Under the conditions of drying paper, it is not likely that the silicious deposit is ever dried below 25 per cent water and it generally carries more than that into the paper.

The solubility of the precipitate in a large amount of water, as in the dilution of stock for the paper machine, is appreciable. When the precipitation was conducted in a solution neutral to litmus the solubility was greater (28.8 per cent of the silica content) than when a slight excess of alum was added (12.9 per cent); with a large excess of alum the solubility was 12.42 per cent, which indicates little advantage from excessive alum.[130-132]

Precipitants Other Than Alum. Precipitants other than alum have been tried [133] but have not come into general use. Magnesium

[128] Blasweiler, Th. E., "Die Verwendung von Wasserglas zum Leimen von Papierstoff," Berlin: Otto Elsner Verlagsgesellschaft, 1922, p. 17.
[129] Blasweiler, Trans. of above by L. W. Codd, "The Use of Sodium Silicate for the Sizing of Paper," London: Constable & Co., Ltd., 1926.
[130] Blasweiler, Th. E., *op. cit.*, German edition, p. 23; *Papierfabr.*, **19**, 809-816, 875-877, 992-997, 1108-1111, 1217-1223 (1921); *Paper*, **28**, No. 22, 20-22; No. 24, 20-22; **29**, No. 6, 19-20; *Paper*, **34**, No. 22, 1011 (1924).
[131] A. R., *Papeterie*, **43**, 1077; **44**, 58-61 (1922).
[132] *Papermakers' Monthly J.*, No. 4, 122-123 (1911).
[133] Klason, *Papier-Ztg.*, No. 34, 1315 (1907).

sulfate [134] gives low yields and the alkalinity of magnesium hydroxide is objectionable in the paper. Mixtures of aluminum and magnesium sulfates have also been tried. Ferrous sulfate was investigated by Carter,[135] who found that the salt would produce satisfactory sizings for dark colored paper. Like alum, it yields smaller precipitates as the amount of water is increased. The most satisfactory results were obtained when rosin size and silicate had been well beaten with the fiber and the ferrous sulfate was added as solid crystals just previous to the discharge of the beating engine. A solution of Carter's which had been kept in a closed vessel over night was found to yield 58 per cent ash. This is probably due to partial oxidation of the iron in solution.

Electric Charge. Pure paper pulp, colloidal rosin, and colloidal silica all bear negative charges. In the case of cellulose, the charge may be reversed by intimate contact with aluminum sulfate.[136] The acidity necessary to reverse the charge on colloidal silica is not reached under any conditions appropriate to paper sizing. Gordon [137] found the charge negative at pH 3.567 and positive at 1.217. The presence of opposite charges may assist in the retention of the silicious precipitate, but simple filtration in the process of forming the sheet of paper also plays a part.

Use of High-Ratio Silicates. In using the higher percentages within the range employed in practice, it will be found that the stock holds water somewhat longer on the wire. This permits better felting of the fibers and is one of the elements in improving strength. This action is not enough to be a disadvantage from an operating point of view in most papers up to 6 per cent $Na_2O,4SiO_2$, 1.3 specific gravity, based on the dry fiber stock. At 10 per cent it is usually appreciable and may necessitate either greater suction or slower operation of the paper machine.

Retention of Filling Materials. As will be seen from Table 87,[138] the use of silicate precipitated in the pulp aids the retention of filling materials and counteracts their tendency to reduce strength.[139, 140, 141]

[134] Frohberg, A., *Wochbl. Papierfabr.,* **44**, 4250-4252 (1913).
[135] Carter, John D., unpublished records of the Philadelphia Quartz Company.
[136] Ostwald, W., and R. Lorenz, *Kolloid Z.,* **32**, 11-76, 119-137, 195-209 (1923).
[137] Gordon, Neil E., Colloid Symposium Monograph, New York: Chemical Catalog Co., **1924**, Vol. 2, pp. 119-121.
[138] Blasweiler, *op. cit.,* German edition, p. 25.
[139] Brit. Pat. 177,137 (Nov. 24, 1921); Fr. Pat. 543,763; and *Paper,* **31**, No. 20 (1920).
[140] *Papeterie,* **41**, 634 (1919).
[141] Altmann, P. E., Ger. Pat. 288,106.

Retention of Colors. So also, silicates may help the retention of colors partly by the mechanical process of filtering them out of the water in which they are suspended with fiber and partly by adsorption of color on the silicate precipitate. Basic dyes are strongly adsorbed, substantive dyes weakly, and acid not at all. Acid dyes therefore wash out. Magnesium sulfate is the best precipitant for holding basic colors; aluminum sulfate is best for substantive colors; and calcium salts are intermediate in both cases. Color lakes of this type have been offered on the market. The retention of silica is best with alum and a basic dye.[142, 143]

Manipulation of Silicate in the Mill.

Rôle of Silicate. The manner of using silicate in paper will depend upon the objects sought and the conditions obtaining in the mill. To illustrate, thin translucent paper known as glassine is made from a stock which is thoroughly hydrated in the beating engine. Silicate should be added early in the operation and left alkaline in order to assist the mechanical treatment which induces the pulp to take up water. It is allowable to do this because the presence of silica so modifies the action of the alkali that it does not injure the strength of the cellulose. Then, shortly before the beater is dropped, alum is added to precipitate silicate and rosin size together.

Very different is the procedure in the case of a cheap writing paper. The beating time instead of several hours may not be more than an hour, and colors sensitive to alkali are often used. Here the silicate must be put into the water with the pulp, and alum for precipitation added as soon as possible to give time for coloring after the silicate has been neutralized.

Or again the principal object of adding silicate may be to increase strength, to retain clay or other filler, or to control a tendency of small fibers to stand up above the surface of the sheet.

Kind of Silicate. As alum is needed to cause precipitation of the silica in proportion to the amount of soda present, the more silicious silicates are usually chosen by the papermaker.

Na_2O, $3.86SiO_2$, 1.3 sp. gr., requires about 25 lbs. papermaker's alum (18% Al_2O_3) for 100 pounds silicate.

Na_2O, $3.3SiO_2$, 1.4 sp. gr., requires about 33 lbs. of alum per 100 pounds silicate.

[142] Heuser and Behr, *Papierfabr.*, 1-6 (1923); *Paper*, **31**, No. 18, 7-12 (1923).
[143] Heuser, *Paper Maker*, **64**, 433 (1922).

TABLE 87. *Pure Mineral Sizing.*

(Blasweiler)

Kind of Sizing	Per Cent Precipitant Based on Air-Dry Filler $Al_2(SO_4)_3$	NaCl	Mineral Sizing Per Cent SiO_2 Related to Total Used	Per Cent SiO_2 Based on Air-Dry Fiber	Strength Length of Strip from Tearing Test Abs.	Gain or Loss by Tearing Test Abs.	Stretch Abs.	Gain or Loss of Stretch
1 5% Silicate 38°Bé.	7.0	...	29	0.36	4460	260	3.46	...
2 10% Silicate 38°Bé.	8.2	...	47	1.20	4500	300	3.40	−0.07
3 10% Silicate 38°Bé.	8.2	...	45	1.16	...	...	...	...
4 10% Silicate, dry	11.0	...	72	5.30	4740	360	3.22	+0.19
5 10% Silicate, dry, 20% China Clay	11.0	...	...	...	3780	...	2.63	1.00
6 20% China Clay, alone	...	...	...	...	...	...	...	...
7 20% China Clay with Al_2O_3	1.8	...	...	...	3220	1500	2.94	0.36
8 10% Silicate, dry, 20% talc	11.0	...	...	...	3610	...	3.15	...
9 20% Talc, alone	...	...	...	...	...	...	...	...
10 20% Talc with Al_2O_3	1.8	...	...	...	3280	358	3.25	+0.10
11 30% Silicate 38°Bé.	17.0	...	...	...	3200	500	1.89	+0.13
12 15% Silicate 38°Bé.	10.0	...	...	...	3440	...	1.45	...
13 15% Silicate 38°Bé., 20% China Clay	10.0	...	...	...	2825	...	1.50	...
14 20% China Clay with Al_2O_3	2.0	...	...	...	2654	...	1.53	...
15 10% Silicate, dry, neutral	8.0	150	60	4.40	...	...	...	...
16 10% Silicate, dry, acid	11.0	150	80	5.90	...	...	...	...
17 10% Silicate, dry, strongly acid	16.0	150	89	6.60	...	...	...	...
18 Metasilicate, as No. 17	7.0	...	41	0.76	...	...	...	...
19 Metasilicate, as No. 4	32.0	...	17	1.23	...	...	...	...

#	Kind of Sizing	Per Cent Filling Material in Paper Based on Total Used	Per Cent Filling Material in Paper Based on Air-Dry Paper	Per Cent Ash in Air-Dry Paper	Capillary Test Rise per Hour Mm. H₂O	Capillary Test Rise per Hour Mm. Printing Varnish	Unsized Fiber Tearing Length	Unsized Fiber Stretch	
1	5% Silicate 38°Bé.	….	….	….	27.0	8.8	4200	3.47	
2	10% Silicate 38°Bé.	….	….	….	30.6	8.7	4200	3.47	
3	10% Silicate 38°Bé.	….	….	….	45.3	8.7	….	….	
4	10% Silicate, dry	….	….	2.56	30.0	10.0	4380	3.03	Sizing with Na₂O,3SiO₂ 38°Bé.
5	10% Silicate, dry, 20% China Clay	61	12.26	13.33	46.3	9.3	3800	3.68	
6	20% China Clay, alone	47	9.31	8.62	40.0	6.2	….	….	
7	20% China Clay with Al₂O₃	50	10.02	9.40	36.0	7.0	4700	3.30	
8	10% Silicate, dry, 20% talc	76	15.12	16.49	34.3	7.60	3638	3.15	
9	20% Talc, alone	57	11.43	10.94	32.0	6.0	….	….	
10	20% Talc with Al₂O₃	61	12.21	11.94	29.66	6.66	3638	3.15	
11	30% Silicate 38°Bé.	….	….	….	40.0	8.0	2700	1.76	
12	15% Silicate 38°Bé.	….	….	4.95	26.0	7.0	….	….	Newspaper
13	15% Silicate 38°Bé., 20% China Clay	90	17.90	20.72	25.0	7.0	….	….	
14	20% China Clay with Al₂O₃	84	16.80	16.00	….	….	….	….	
15	10% Silicate, dry, neutral	….	….	….	….	….	….	….	
16	10% Silicate, dry, acid	….	….	….	42.0	7.0	….	….	Salted out with NaCl
17	10% Silicate, dry, strongly acid	….	….	….	….	….	….	….	
18	Metasilicate, as No. 17	….	….	….	….	….	….	….	Metasilicate sizing
19	Metasilicate, as No. 4	….	….	….	31.0	7.2	….	….	

The silicate used was Na₂O, 3.3SiO₂

Technic. Silicate may be manipulated to avoid interfering with colors, and it may with advantage be used wherever hydration is desirable and an increase of ash permissible. Wherever hardness or smooth surface is sought silicate sizing will help but often at some sacrifice of bending properties. The balance between these opposing tendencies will often determine the amount of silicate to be added. Mills making the most various kinds use from 2 to 10 per cent.

The texture of a silicate precipitate depends on the dilution of the silicate and the alum. Under the conditions occurring in the beater a light flocculent product, well adapted to harden and increase the strength of the paper, is produced, but if the chemicals were mixed in relatively concentrated condition the material thrown out would be granular, sandy, or lumpy, just as would be the case if dry alum were mixed with a strong solution of rosin size. When the light flocculent precipitate is dried, it hardens to a horny consistency, too hard to be crushed easily by the hand. In this hard condition it still retains a considerable amount of water, which contributes largely to its toughness.

Effects of the Silicate. The effect of retaining this material in the substance of paper is shown first of all by an increase in the ash of the paper.[144] A study involving 550 tons of paper and an examination of 1,200 samples gave an average of 1 per cent in ash with an average addition of 3.48 per cent of liquid silicate based on dry fiber. The amount of dry alum necessary for the precipitation of the silicate was 25 per cent of the weight of the silicate solution. The average retention was 66 per cent of the total silica in the silicate, plus the Al_2O_3 of the alum. There is good reason to suppose that the use of larger proportions of silicate would not only produce more marked effects on the paper but would be accompanied by a higher percentage retention.

The hardness and the finish of the paper were determined by the combined judgment of several experienced papermakers, as there was no method of reducing these qualities to a numerical standard. From comparison of sheets, which differed only by the silicate content and the alum requisite for its precipitation, the statement is warranted that the use of silicate in every case produced a harder and a smoother sheet. The Mullen tests of the papers in this series when averaged showed a gain of 12 per cent in favor of the papers containing silicate. Ink resistance was studied in four different grades of paper by the floating method with standard ink. In one case the silicated sheets gave the same values as those with rosin sizing only, but in three of these grades

[144] Furness, Rex, *Paper-maker & Brit. Trade J.,* **73,** 107 (March 1, 1927).

the papers containing silicate showed better ink resistance than those which contained none. This may be attributed to the increased retention of rosin in the paper, there being no reason to believe that sodium silicate can of itself increase the resistance of paper to water or to an aqueous ink.

In studying the effect of the addition of silicate to the beater, it was observed that the increment of ash increased over a period of several hours, sometimes reaching its maximum as late as 7 hours after stock containing silicate came on the machine. This is interpreted to mean that a larger precipitation of the silicate and better retention develop as the white waters from which the silicate has been precipitated are returned to the machine and to the beaters.

The higher retention of the silicate precipitate is not wholly due to the accumulation of silica in the water, but it has been shown experimentally that prolonged agitation increases the amount of precipitate even in the absence of pulp. Thus it may be expected that those papers in which the manufacturing routine provides a long beating will not only retain the silicate better on account of closer texture of the sheet, but will also have the advantage of more complete precipitation of the silica. This is of minimum importance in those mills where most of the water is saved for recirculation, but may be very significant where beating time is short, or where the mill works but a few hours on one kind of paper.

Trimmings Put to Use. The waste of the fiber container industry consisting of trimmings from the manufacturing process and of containers which have served their intended purpose provides a large amount of stock to paper mills. The silicate used as adhesive in this stock may now be turned to good account by precipitating it with alum and making a better finished paper board. Though silicate which is not neutralized is detrimental to rosin sizing, these clippings, which may contain 7 per cent by weight yield a satisfactory surface when this is properly precipitated.[145]

COMBINATIONS WITH SOLUBLE SILICATES.

Rosin Saponified by Silicate. Blasweiler, who worked under the authoritative guidance of Emil Heuser, also studied the use of soluble silicates in conjunction with other colloids for sizing paper. He found that the proposals to make concentrated size by using silicates to saponify rosin at low temperature offered little advantage over the ordi-

[145] Vail, James G., *Fibre Containers*, **6**, No. 8, 16 (1921).

TABLE 88. *Silicate and Rosin.*

(Blasweiler)

Kind of Sizing	Per Cent $Al_2(SO_4)_3$ Crystal-line, Based on Air-Dry Fiber	Per Cent SiO_2 in Paper Related to Total Used	Per Cent SiO_2 in Paper Based on Air-Dry Fiber	Strength — Length of Strip from Tearing Test, Abs.	Strength — Gain or Loss by Tearing Test*	Per Cent Stretch Abs.	Gain or Loss of Stretch*
1 3% Rosin	3	...	...	3990	+190	3.85	+0.17
2 0.5% Rosin, as free colloidal rosin	2	..	...	3990	+180	3.44	...
3 0.5% Rosin, with NaOH, cold, saponified in the cold, 5% Silicate 38° Bé	5	43	0.57	....	...	...	...
4 0.5% Rosin, saponified with 20 times that amount of Silicate 38° Bé	6	30	0.91	3800	+160	3.55	+0.40
5 As in No. 4, + 20% China Clay	6	...	...	3340	−300	3.13	...
6 3% Rosin + 20% China Clay	3	...	...	3100	−1200	3.31	−0.30
7 0.5% Rosin saponified with 20 times that amount of Metasilicate	41	54	6.10	2300	−1300	2.09	−1.06
8 1% Rosin + 5% Silicate 38° Bé, according to Sommer, Ger. Patent 257,816	5	59	0.75	....	...	...	...
9 1% Rosin + 5% Silicate, dry, according to Sommer Patent	7	62	2.29	....	...	...	...
10 0.5% Rosin + 5% Silicate, dry, according to Sommer Patent	8.2	..	...	4260	+ 60	3.00	−0.47

*Compared with unsized fibers.

No.	Kind of Sizing	Per Cent Filling Material in Paper Based on Total Used	Per Cent Filling Material in Paper Based on Air-Dry Paper	Per Cent Ash in Air-Dry Paper	Capillary Test Rise per Hour Mm. H_2O	Capillary Test Rise per Hour Printing Varnish	Unsized Fiber Tearing Length	Unsized Fiber Stretch	Notes
1	3% Rosin	..	..	0.81	0.0	7.0	3800	3.68	
2	0.5% Rosin, as free colloidal rosin.....	..	..	....	0.0	7.0	....	...	
3	0.5% Rosin, with NaOH, cold, saponified in the cold 5% silicate 38° Bé.....	..	..	....	...	...	....	...	Rosin and $Na_2O, 3SiO_2$
4	0.5% Rosin, saponified with 20 times that amount of Silicate 38° Bé.......	..	..	2.82	5.0	7.0	3640	3.15	
5	As in No. 4, + 20% China Clay	66	13.15	14.19	11.0	7.0	3640	3.15	
6	3% Rosin + 20% China Clay	62	12.45	11.78	0.0	7.5	4300	3.61	
7	0.5% Rosin saponified with 20 times that amount of Metasilicate	..	..	....	...	...	3640	3.15	Rosin and metasilicate
8	1% Rosin + 5% Silicate 38° Bé. according to Sommer Patent	..	..	....	...	...	....	...	
9	1% Rosin + 5% Silicate, dry, according to Sommer Patent......	..	..	....	...	...	....	...	Ger. Patent 257,816
10	0.5% Rosin + 5% Silicate, dry, according to Sommer Patent......	..	....	....	21.1	7.2	4200	3.47	

The Silicate used was $Na_2O, 3.3SiO_2$.

nary practice of using rosin size and silicate separately.[146, 147]   Even
when immediate precipitation of silica is avoided the size tends to de-
posit silica on dilution before the addition of alum. Saponifying in dilute
solution immediately before addition to the pulp gave better retention
of silica and some gain in strength.[148]

Other Materials. Fatty acid soaps have also been used in sizing
paper. They are compatible with soluble silicates and adapted to give
water-resistance with better bending properties than rosin.[149, 150, 151]
Bakelite has been used, but its advantages over rosin are not commen-
surate with the present difference in cost.[152, 153]

The advantages of increased retention of other colloidal sizing ma-
terials are had when silicate sizing is used in conjunction with animal
glue, casein, montan wax, or starch.[154-162]

Silicates and Starch. Starch, in particular, when heated in a sili-
cate solution until it swells becomes involved in the silicate precipitate

TABLE 89. *Sizing with Silicate and Starch.*
(Blasweiler)

Kind of Sizing	Strength Figures with Starch		Without Starch		Increase in Tearing Strength		+ or − Tearing Strength
	Tearing Length	Stretch	Tearing Length	Stretch			
	mm.	%	mm.	%			
5% swollen starch......	3800	3.68	4150	3.76	350	9.2	+0.08
5% swollen starch, ppt..	3800	3.68	4350	3.40	550	14.5	−0.20
10% swollen starch, ppt.	3800	3.68	4550	3.80	750	21.5	+0.12
10% raw starch and 10% sodium silicate, 38°Bé., ppt.	3650	3.15	4300	3.50	650	17.8	+0.35
5% starch, 5% sodium silicate, 38°Bé., ppt...	3650	3.15	4280	3.67	630	17.3	+0.52
10% starch, 10% sili- cate, 38°Bé., swollen, ppt.	3650	3.15	4600	3.48	950	26.0	+0.33

The silicate used was $Na_2O, 3.3SiO_2$

[146] Kuldkepp and Graf, Ger. Pat. 245,975 (Oct. 20, 1909).
[147] Clapp, Albert L., U. S. Pat. 1,345,317 (June 29, 1920).
[148] Sommer, George G., Ger. Pat. 257,816 (Aug. 20, 1911).
[149] Kolb, *Papierfabr.,* **19,** 1141-1144 (1921) ; *C. A.,* **16,** 493.
[150] Blasweiler, *loc. cit.*
[151] West, Clarence J., *Ind. Eng. Chem.,* **14,** 858-860 (1922).
[152] Holzverkohlungs-Industrie Akt.-Ges., Ger. Pat. 338,396 (1921).
[153] West, Clarence J., *Paper Trade J.,* **73,** No. 15, 52 (1921).
[154] Clapp, Albert L., U. S. Pat. 1,592,294 (July 13, 1926).
[155] Müller, Ger. Pat. 317,948 (1920).
[157] Possanner, E., *Chem. Ztg.,* **38,** 100 (1914).
[158] Ger. Patents reviewed by West, *Paper Trade J.,* **75,** No. 1, 55 (1922).
[159] Mosley, J. F., Brit. Pat. 226,850 (Aug. 24, 1923).
[160] Reichard, F., Brit. Pat. 177,137 (Nov. 24, 1921).
[161] See also Fr. Pat. 543,763: *Paper,* **31,** No. 20 (1920).
[162] Altmann, P. E., Ger. Pat. 288,106.

in such an intimate way that the retention is increased, 60 to 70 per cent of that used being found in the paper.[163]

Silicate which has been boiled with starch and precipitated with alum exhibits a horny texture quite different from the corresponding precipitate without starch. Although raw starch is flocculated by alum it is poorly retained in paper, but it imparts a pleasing finish and is used in numerous mills. Whether viewed as a modification of silicate sizing with starch in minor proportion or as a means of retaining starch with silicate in the lesser rôle, the combination is a useful tool in the hands of the skilled papermaker.[164-167]

Advantages of Silicate Sizing.

From an operating point of view the advantages of silicate sizing include :

1. Good formation of the sheet and satisfactory removal of water by suction.
2. No sticking on the press rolls.
3. As a result of the above, increased life of the felts.
4. Quick and complete sedimentation of the white waters.
5. Increased retention of filling materials without sacrifice of strength.
6. Economy in coloring.

In addition, the qualities imparted to the paper, though they vary according to the kind of stock and method of manipulation, may be summarized :

1. A small though definite increase in strength. This is of the order of 10 per cent.
2. Increase of rattle or snap of the paper.
3. Better feel—i.e., a smoother surface free from protruding fiber ends.
4. The combination of quick absorption of printers' ink with hardness which makes a clean impression for offset and other rapid printing processes.
5. Reduction of the tendency of cut sheets to curl.

The kinds of paper in which silicates are being used include a wide range, but a few are listed with the principal advantages sought.

Bristol board .... stiff smooth surface, generally with starch and rosin.
Kraft .... increased strength and reduction of mechanical treatment to affect hydration.
Book .... clay or talc retention without loss of strength.
Envelope .... small amounts to improve finish.
Straw .... denser, stiffer sheet, low cost.[168]
Greaseproof .... better hydration.
Glassine .... same to increase transparency.
Writing .... better finish and formation.

[163] Lutz, Alfred, "Ber. d. Hauptvers. d. Vereins d. Zellstoff und Papier Chemiker," **1907**.
[164] Blasweiler, Th., *Wochbl. Papierfabr.*, **56**, 89-93 (June 13, 1925).
[165] Fues, *Wochbl. Papierfabr.*, **44**, 835-841, 1223 (1913).
[166] Wrede, Hans, *Wochbl. Papierfabr.*, **44**, No. 10, 835 (1913); *C. A.*, **7**, 2114.
[167] Wrede, Hans, *Papierfabr.*, trans. in *Paper*, **31**, No. 12, 11-14 (1923); *Papierfabr.*, **23**, No. 18, 293 (1925).
[168] *Papeterie*, **43**, 1077; **44**, 58-61 (1922).

TABLE 90. *Sizing With and Without Silicate.*

(Blasweiler)

Silicate Sizing	Strength	Filler	Unsized Material — Raw Material Strength	Unsized Material — Raw Material and Filler Strength	Unsized Material — Raw Material and Filler Filler	Sizing Without Silicate	Strength	Filler
Pure Silicate Sizing								
5% silicate 38°Bé.	106	...	100	...	...	3% rosin as free rosin emulsion	105	...
10% silicate 38°Bé.	107	...	100	...	...	3% rosin as free rosin emulsion	105	...
10% silicate, dry	109	...	100	...	...	3% rosin as free rosin emulsion	105	...
10% silicate, dry, + 20% china clay.	100	130	100	100	100	2% $Al_2(SO_4)_3$ Aq. + 20% china clay	68	107
10% silicate, dry, + 20% talc.	100	133	100	100	100	2% $Al_2(SO_4)_3$ Aq. + 20% talc.	90	107
30% silicate 38°Bé.	119	...	100	...	...	2% $Al_2(SO_4)_3$ Aq.	106	...
15% silicate 38° Bé, + 20% china clay	106	107	100	100	100	Newspaper — 2% $Al_2(SO_4)_3$ + 20% china clay	100	100
Silicate and Rosin								
0.5% rosin soap with silicate equivalent to 11.6% 38° Bé silicate	104	...	100	...	...	3% rosin as free rosin emulsion	100	...
0.5% rosin soap with silicate equivalent to 11.6% 38° Bé silicate + 20% china clay	92	140	100	100	100	3% rosin as free rosin emulsion + 20% china clay	75	132
Silicate and Fatty Acid								
0.5% soya bean oil as Na-soap + 5% silicate, 38°Bé.	102	...	100	...	...	0.5% soya bean oil as Na-soap	94	...
0.5% cottonseed oil as Na-soap + 5% silicate, 38°Bé.	100	...	100	...	...	0.5% cottonseed oil as Na-soap	94	...
5% cottonseed oil as Na-soap + 15% silicate, 38°Bé.	105	...	100	...	...	0.5% cottonseed oil as Na-soap	57	...
0.5% soya bean oil	100	...	100	...	...	0.5% soya bean oil as Na-soap	94	...

Silicate and Animal Glue

Silicate treatment						Base material
2% animal glue + 10% silicate 38° Bé	124	...	100	122	...	2% animal glue
2% animal glue + 10% silicate, 38° + 20% talc	97	132	100	96	117	2% animal glue + 20% talc

Silicate and Starch

Silicate treatment						Base material
5% starch swollen with 5% silicate, 38°Bé.	117	...	100	114	...	5% swollen starch
10% starch swollen with 10% silicate, 38°Bé.	126	...	100	120	...	10% swollen starch
5% starch swollen with 5% silicate, 38° Bé. + 20% china clay	...	149	100	...	130	5% swollen starch + 20% china clay
10% starch swollen with 10% silicate, 38° Bé. + 20% talc	...	146	100	...	130	10% swollen starch + 20% china clay

Silicate and Casein

Silicate treatment						Base material
1% casein dissolved with 5% silicate, 38°Bé. + 20% china clay	...	140	100	...	111	1% casein in ammoniacal solution and 20% china clay

Explanation:—The tearing lengths of the unsized and unloaded basic materials are set to equal 100. Likewise the amounts of filling material remaining in the paper, with unsized but loaded materials are equal to 100. The other numbers give the relation of the tearing lengths and loading material values. The silicate used was $Na_2O, 3.3SiO_2$.

Any printing paper which is not required to withstand aqueous inks may be made without the danger of discoloration which is characteristic of all rosin sized papers on long exposure to light.

Textile Processes.

Silk Weighting.

Reason for Weighting. Silk weighting has been referred to as a "nefarious practice",[169] but the public view of substituting one substance for another is in process of change, and recently advertisements have appeared in which the advantages of weighted silk are set forth.[170]

The moral aspect is no longer a matter of concern when the buyer knows what he is purchasing, and the seller points out its advantages with candor. There can be no question that the weighting of silk has been carried in some cases to a point where its value was much depreciated. It is also true that some properties useful in the making of certain textiles, notably ribbons, are imparted by weighting. The better draping qualities of weighted fabrics is often a determining factor. We are here concerned only with the process which employs soluble silicates.

Method. Raw silk contains a soluble gum which accounts for 18 to 25 per cent of its weight. This is first more or less completely removed in a soap solution. The weighting is done in a 28° Baumé, 1.239 specific gravity, solution of tin chloride, containing 0.5 to 1.5 per cent free hydrochloric acid, which is kept cold. The treatment continues for an hour during which time the silk gains 12 to 15 per cent in weight.[171] Cotton under similar treatment would gain 0.5 to 2 per cent. The mechanism of the reaction is not known. It was thought to be a matter of hydrolysis, but as the silk will take up 11 to 12 per cent of stannic chloride from an anhydrous solution in benzol, this is plainly not the whole explanation. Stannic chloride forms compounds with amino acids, and a similar process may take place in the silk. Hydrolysis of course takes place in the washing which is the next step, so that stannic hydroxide is present when the silk is put into a 5° Baumé, 1.036 specific gravity, solution of disodium hydrogen phosphate at 54°C. (130°F.) and worked for an hour. This cycle may be repeated according to the weight desired, each pass through tin and phosphate baths adding about 15 per cent to the weight of the silk.

[169] Encyclopedia Britannica, 11th ed., vol. 25, p. 103.
[170] Advertisement in *Silk Journal*, Textile Dyeing Co. of America (1927).
[171] Roscow, James, U. S. Pat. 1,602,840 (Oct. 12, 1926). *Cf.* McDowell, Joseph Curry, U. S. Pat. 1,558,104 (Oct. 20, 1925).

The silicate is used as a single final treatment at 5° Baumé, 1.036 specific gravity, and 65°C. (140°F.). The weight added by the silicate depends upon the amount which the tin and phosphate baths have put in.[172, 173] Two passes of these enable the silicate to add 12 to 15 per cent, 3 passes about 20 per cent, and 4 passes up to 30 per cent.

Aluminum sulfate may be used after the tin and phosphate baths to further increase the weight. The silk is made acid with a 5 to 8 per cent solution of sulfuric acid and worked in a 3.5° to 4.5° Baumé aluminum sulfate bath at 35°C. and finally in a silicate bath of 4° Baumé, 42°C. The extent of weighting by this method is dependent upon the amount of tin phosphate in the silk as well as upon the details of manipulation. Increase of concentration or temperature of the silicate makes for greater weight. So does longer time of treatment, but skill is essential to obtain silk of proper strength and free from any trace of flocculent deposit which would cause dyes to take unevenly. The silicate should never be used above 63°C. (145°F.). A final process to increase weight which has come out below expectations is to put silicate 1.5 times as heavy as the silk to be treated in a 10 per cent soap solution and treat the silk for an hour at 42°C. As much as 15 per cent can be added in this way. It is necessary to add more weight than is expected in the finished silk as some is lost in the dyeing or bleaching processes which follow. This may amount to 20 per cent. Details of technic are set forth by Ley [174] with elaborate precautions essential to success in this complicated and difficult art. He also describes a combination of cutch and logwood weighting with tin phosphate and silicate.

A total weighting up to 50 per cent of the boiled-off silk seems to have very little influence on strength and 100 per cent weighting is suitable for many purposes. Ribbon silks are often weighted up to 250 per cent on the basis of fiber after removal of gum.

As the process plumps the fiber and improves its luster and feel, it is generally used for such goods as hosiery and ribbons. This gives a better result than the thin fibers of untreated silk.

The procedure may be varied to permit weighting either in skeins or as woven or knit goods. An increasing amount of silk is now weighted in the piece.[175-177] Mayer says that it is almost universal in Germany,

[172] Knup, J., Brit. Pat. 6,728 (1904).
[173] Weidmann, U. S. Pat. 780,924 (1905).
[174] Ley, Hermann, "Die Neuzeitliche Seidenfärberei," Berlin: Springer, 1921.
[175] Rossbach, Helmut, *Deut. Farben Ztg.*, 57, 586-587 (1921) ; *C. A.*, 15, 3754.
[176] Trotman, S. R., *Textile Recorder*, 25, 46-49 (1924), reprinted in *Dyestuffs*.
[177] *Posselt's Textile J.*, 29, 111-132 (1921).

where the mineral content of silk frequently runs from 40 to 75 per cent, of which 40 per cent may be silica.[178-182]

The great mass of moderately weighted silk performs its intended function without difficulty and gives complete satisfaction at a cost not to be attained with the pure fiber.[183]

The industry has reached substantial proportions in this country, having consumed in 1922, approximately 6,250 tons.

Requirements of the Silicate. Silicate for silk weighting is required to be crystal clear, and because the life of the treating bath is terminated by the appearance of silicious floc which would cause dyes to take unevenly if deposited on the outside of the fiber, it should be as stable as possible. A good test is to reduce the concentration to 5° Baumé, boil for five minutes and allow to stand for an hour, at the end of which time it should be clear and free from floc. The ratios used in the industry vary from $Na_2O, 2.4SiO_2$ to $Na_2O, 3.3SiO_2$, the more alkaline being preferred, as the silk or the precipitate formed in the silk adsorbs sodium in a manner analogous to other silicious precipitates. Some of this is removed from the silk during washing, but the bath eventually becomes unstable and must be discarded.[184]

Color. Many acid colors which are popular on pure silk are not readily adsorbed by tin-weighted silk and require great care in manipulation. Basic dyes are easily applied on tin-weighted silk. Very heavy weighting followed by exposure to sunlight may cause the fiber to become tender. In some cases, reddish colored spots appear which may be guarded against by a treatment with weak ammonium thiocyanate. Tendered silk is restored by treatment with hydrofluoric acid.[185]

Test for Weighting. The presence of mineral weighting is easily detected by burning a strip of silk. Pure silk burns completely, and heavily weighted goods leave a white skeleton of ash. A quick quantitative method consists in comparing X-ray photographs of weighted silk with those of standard samples.[186] A more exact procedure is based on extraction with 2 per cent hydrofluoric acid at 60°-70° for 20

[178] Mayer, Hermann, "Das Wasserglas," Sammlung Vieweg, No. 79, **1925**, Braunschweig: Friedr. Vieweg & Sohn Akt.-Ges.

[179] Neuhaus, Ger. Pat. 75,896 (Jan. 25, 1893); 305,275, 305,770.

[180] Keiper, *Melliands Textileberichte*, **3**, 181 (1922).

[181] Heermann, *Chem. Ztg.*, **35**, 829 (1911).

[182] Sisley, *Chem. Ztg.*, **35**, 621-622 (1911); *C. A.*, **6**, 158.

[183] Dyestuffs, **26**, No. 11, 167 (1925).

[184] Cole, George Warren, Jr., Fr. Pat. 562,658 (Feb. 23, 1923).

[185] *Textile Colorist*, **26**, 167 (1925).

[186] Tondani, Carlo, *Giorn. chim. ind. applicato*, **4**, 17 (1921); *C. A.*, **16**, 1872.

minutes followed by 2 per cent sodium carbonate at 60°-65° which removes the tin-silicate weighting.[187]

Dyeing and Printing.

Mordants. Silicate solutions are effective as fixing agents for iron and chromium salts used as mordants, especially the arsenates and phosphates, which are rendered insoluble in a bath of one of the more silicious grades. Colloidal silica itself serves as a mordant for aniline green. The fiber is prepared by passing through a silicate bath followed by a weak acid.[188-193] Dilute silicate baths protect cotton dyed with sulfur colors, which sometimes develop enough acidity to cause hydrolysis and weakening.

Printing. In textile printing, silicates serve where a viscous alkaline medium is required to apply a color or reagent in such condition that the design shall remain clear and sharp.[194] Particularly is it useful in the application of vat colors, where they are not only cheaper but give better results than potassium carbonate which is often recommended.

After indigo has been discharged with hydrosulfite and the goods have been washed, a silicate bath will brighten the white parts of the pattern without risk of weakening the goods. It is also said to brighten colors.[195, 196] At least, experience in washing shows that silicate has a protective action as a result of which colors of washed goods are brighter than when soap only is used to cleanse them. Silicate precipitated locally in the fiber by a printing process previous to dyeing yields shaded figures.[197]

Alkaline Reagents. Silicate solutions, on account of the buffer action of the silica which prevents too great activity of the alkali, are chosen as alkaline reagents in various textile processes. Their action can be further regulated by additions of sodium chloride or sodium

[187] Cook, A. A., *Textile World*, April 15, 65-67; May 22, 131-133 (1922); *C. A.*, **16**, 2782-2783.

[188] Bolley, *Chem. Gazette*, **13**, 58-59 (1855).

[189] Favre, Camille, *Z. angew. Chem.*, **19**, pt. 2, 1476 (1906).

[190] Göbels, Albert, *Neueste Erfindungen und Erfahrungen*, **17**, 18-20 (1920).

[191] Joclét, Victor, "Die Kunst und Feinwäscherei in ihrem ganzen Umfange," **63**, 3rd ed., Wien: Hartleben's chemisch-technische Bibliothek, **1879**.

[192] Joclét, Victor, "Die Woll und Seiden Druckerei in ihrem ganzen Umfange," **46**, Wien: *Hartleben's chemisch-technische Bibliothek*, **1879**.

[193] Knecht, Rawson and Lowenthal, "A Manual of Dyeing," **1**. Philadelphia, Pa.: Lippincott, **1910**, p. 203.

[194] Soxhlet, V. H., "Die Praxis der Anilin-Farberei und Druckerei auf Baumwollwaaren," Wien: *Hartleben's chemisch-technische Bibliothek*, **184**, (1890).

[195] *Deut. Farben. Ztg.*, abstract in *J. Soc. Chem. Ind.*, **1**, 279 (1882).

[196] Grüne, W., *Deut. Musterztg*, No. 6 (1854); *Chem. Zentr.*, **26**, 71-74.

[197] Kasuya, Saburo, Jap. Pat. 40,695 (Nov. 18, 1921); *C. A.*, **17**, 1893.

sulfate. Thus cellulose acetate and cotton may with advantage be dyed in silicate baths.[198, 199]

SIZING.

The art of textile sizing and finishing makes incidental or rather specialized use of silicate solutions to modify other colloids which are the basic materials of the art. Starches, dextrins, gums, glues, clays, and other fillers are all compatible in appropriate proportions with soluble silicates as appears from discussions of adhesives and other uses where the silicates of soda play a larger part.[200, 201]

Sizing materials in contrast to adhesives should be able to penetrate the surfaces on which they are laid,[202-204] which suggests that silicates should not be used at high concentrations. Some sizes are made with silicate and a precipitant such as aluminum sulfate, liberating silica, which plays the rôle of filler and gives to the size the combination of high viscosity and penetrating power.

Numerous mixtures which contain silicate[205] have been proposed for textile sizing and finishing processes, a region in which the art has run far ahead of the science. The starches and gums used are for the most part miscible[206-209] with silicate.

MERCERIZING.[210]

A mixture of sodium hydroxide, 28°Baumé, 100 parts, and silicate of soda, 1.39 specific gravity (41°Baumé), 10 parts, was investigated by Hübner and Pope[211] with respect to claims that it would mercerize cotton without tension. They found that the luster of the fiber, though increased, was much less than with a pure sodium hydroxide solution. The shrinkage was less and the affinity for coloring matters was increased. This is a very clear bit of evidence of the restraining action of silica upon the caustic alkali.

[198] Richardson, L. G., Brit. Pat. 175,846 (Dec. 18, 1920); *C. A.,* **16,** 2230.
[199] Dorr, G., *Riv. gen. mat. color.,* **18,** 101-102; *C. A.,* 2950-2951 (1914).
[200] For example, Walen, Ernest D., U. S. Pat. 1,587,094 (June 1, 1926).
[201] Whewell, W. H., *Text. Inst. J.,* **2,** 43 (1911).
[202] *Posselt's Text. J.,* **25,** 53-54 (1919).
[203] Feary, N. A., Brit. Pat. 128,691 (1919).
[204] Poulson, A., Brit. Pats. 165,365 (Sept. 24, 1920); 169,103 (Sept. 24, 1920).
[205] Taylor, Alfred, U. S. Pat. 52,906 (Feb. 27, 1866).
[206] Pickard, R. H., *J. Text. Inst.,* **10,** 54-55 (1919); *J. Text. Inst.,* **9,** 18-22 (1918).
[207] Lamb, M. C., and A. Harvey, *J. Soc. Dyers Colourists,* **33,** 19-20 (1917).
[208] Mayer, *op. cit.,* p. 42.
[209] Polleyn, F., "Die Appreturmittel und ihre Verwendung," **134,** 2nd ed., rev., Wien: Hartleben's chemische-technische Bibliothek, **1897;** "Dressings and Finishings for Textile Fabrics," translated from the German ed. by Charles Salter, London: Scott, Greenwood, **1911.**
[210] Meister, Lucius, and Brüning, Brit. Pats. 10,784, 11,313 (1897).
[211] *J. Soc. Chem. Ind.,* **23,** 409 (1904).

DEGUMMING SILK.

Silicate solutions have been successfully used for boiling off or de-gumming silk, usually in combination with sulfonated oils. Properly controlled, they can displace part or all of the olive oil soap usually employed, with a substantial saving in cost.[212]

[212] *Textile World,* **71,** No. 1, 59 (1927).

Chapter X.

Deflocculation and Detergency.

CHARACTERISTICS OF SOLUBLE SILICATES WHICH AFFECT THEIR DETERGENT ACTION

The suitability of silicate solutions for various detergent uses has been for many years a matter of active controversy. The colloidal phenomena which constitute the familiar processes of washing have engaged the attention of some of the ablest investigators of modern times. A great deal has been learned, enough to show that it is not yet possible to determine with precision the best and most economical materials and technic for washing. It is beyond the scope of this treatise to deal with washing procedure and the problem of selecting washing materials, but it may be possible to sift fact from fancy by considering separately some of the actions of soluble silicates which bear upon the study of washing and to view at the same time other industrial uses which depend upon characteristics which have a part in detergent action.

The opinion of Vincent [1] that a mixture of 80 per cent silicate and 20 per cent soap has merit for general use as a detergent is worthy of careful scrutiny, for it is based upon extensive scientific work. Let us examine the factors one at a time.

DEFLOCCULATION.

Rate of Sedimentation of Clay. The sedimentation of clay from water may be greatly delayed by small additions of alkaline compounds, among them the soluble silicates. Other materials of small dimensions are similarly suspended. The deflocculation is accompanied with a reduced viscosity of the suspension and this facilitates the removal of impurities which exist in particles of larger size than the clay substance or which are less affected by the dispersing action of the silicate than is clay. Quartz, feldspar, siderite, pyrite, ilmenite, biotite, mica and ferric oxide are thus separated, in some cases quantitatively, by settling, after which the clay can be recovered by long settling or more

[1] *J. Phys. Chem.*, **31**, 1305 (1927).

rapidly by a chemical treatment to cause flocculation, as, for instance, neutralizing the silicate with acid.[2] This is in accord with Stokes' law:
$$V = \frac{2r^2 g}{9K\,(d - d^1)},$$ in which V = velocity of settling, r = radius of particles, K = viscosity, d^1 = density of fluid, d = density of particles, and g = gravity constant. Viscosity is the primary factor in the rate of sedimentation when the radius is constant.

Bleininger considers the physical changes to be complex and postulates the formation of a lyophile pseudo-emulsoid substance resulting from the subdivision of clay particles under the influence of hydroxyl ions.[3] When silicates are used, the silica constitutes such a substance which may tend to prevent further decrease of viscosity and thus further delay the settling of fine particles.

Effect of Silicate on Viscosity of Clay Suspensions. If this is the correct conception, it follows that different clays with different
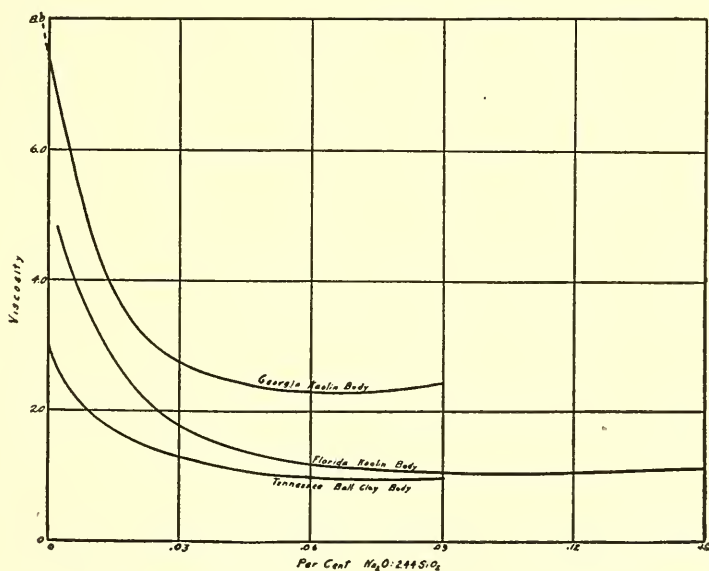
Fig. 139.—Effect of Silicate on Viscosity of Clay Suspensions.

assortments of particle sizes and different degrees of adherence between particles to be dispersed will behave quite differently in the presence of alkali, and so it is. Measurements of viscosity of relatively concentrated suspensions of clay in water show that the addition of silicate solutions causes a rapid drop in viscosity, which is much greater per unit of added Na_2O than when viscosity is lowered by sodium car-

[2] Bleininger, A. V., *Bur of Standards Tech. Paper* No. **51** (1915) ; U. S. Pat. 1,528,908 (Mar. 10, 1925).
[3] Shorter, S. A., *J. Soc. Dyers Colourists*, **34**, 135-138 (1918).

bonate. Even on a weight-for-weight basis the silicate is more effective in some cases and the range of minimum viscosity is wider.

The reduction of water made possible by the lower viscosities makes it possible to produce by casting processes bodies of improved density with decrease of losses from shrinkage cracks and with greater mechanical strength. Another interesting application of this property is in adding clay to soap.[4] Tensile tests show that the point of maximum deflocculation is not necessarily the point of greatest strength, but the following table shows the advantages of reagents and indicates that silicate solutions can produce useful results.

TABLE 91. *Tensile Strength of Castings.*
(Bleininger)

Body Containing as Clay	Without Reagents (kilos per sq. cm.)	Na₂CO₃ Max. Defloccu-lation (kilos per sq. cm.)	Na₂CO₃ Less than Max. Defloccu-lation (kilos per sq. cm.)	Silicate Max. Defloccu-lation (kilos per sq. cm.)	Silicate Less than Max. Defloccu-lation (kilos per sq. cm.)
North Carolina kaolin....	1.063	1.262	0.985	1.034	1.25
Georgia kaolin	4.77	6.14	5.52	7.10	6.3
Tennessee ball clay.......	7.17	10.8	9.65	11.75	9.25
Florida kaolin	4.62	4.95	4.44	3.97	4.39
Body B	...	4.76	5.18	4.15	6.4

This fact is generally recognized in the ceramic industry * and most cast wares are made from clay suspensions in which the viscosity has been reduced by silicate either alone or combined with sodium carbonate.[5] Mixtures of clay and water are subject to changes in viscosity, and those slips which have been liquefied by alkalies, although they are more stable, tend to thicken or become further deflocculated on standing. These changes are reduced when some excess above that required for maximum deflocculation is used. Reactions which take place slowly may change the concentration of hydroxyl ions, but the buffer effect of silicate will tend to hold it nearer constant.

The effect of the reagents, used to reduce the viscosity of clay slips, upon the plaster molds in which the ware is cast has been considered by Kall,[6] who found that reaction between sodium carbonate and calcium sulfate could lead to serious pitting and eventual disruption as concen-

[4] See Feldenheimer, Wm., and W. W. Plowman, U. S. Pat. 1,321,516 (Nov. 11, 1919).
* Other materials may be deflocculated at the same time; for example, see Bellamy, Harry T., U. S. Pat. 1,585,010 (May 18, 1926).
[5] Vail, James G., *J. Am. Cer. Soc.,* **6**, No. 4, 610 (1923).
[6] Kall, G. A., *Sprechsaal,* **60** (1), 8-9 (1927).

tration increased with repeated absorption of the liquid part of the slip and drying for a fresh cycle. He observed, however, that sodium silicate solution ($Na_2O,2SiO_2$) had no deleterious effect upon the molds up to a concentration of 0.5 per cent in the clay. This may be partly due to a tendency of the silicate to remain at the surface of the mold and partly to a smaller tendency to reaction under the conditions of this
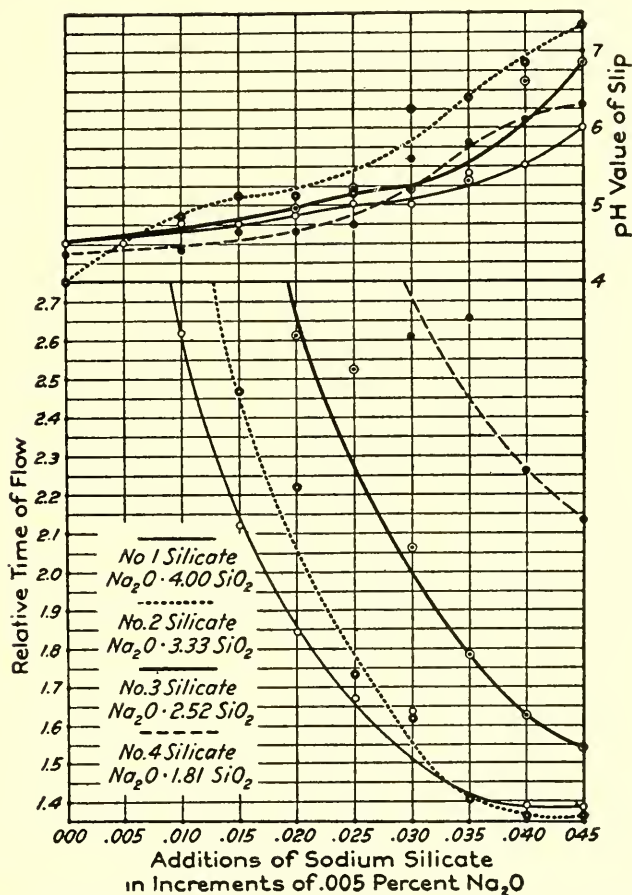
FIG. 140.—Effect of Ratio of Silicate on Viscosity and pH of Clay Slip (McDowell).

use. It should further be pointed out that a more silicious ratio would not only deflocculate better but, containing more colloidal silica, would be still less likely to corrode the plaster molds. Kall recommends that additions of Na_2CO_3 should not be more than 0.1 per cent and that where more liquefying effect is needed it should be obtained with silicate. It is not seen why silicate should not be used in the first instance.

Effect of Varying Ratio on Deflocculation. McDowell[7] has studied the effect of silicates of varying ratio upon deflocculation of a

[7] *J. Am. Ceram. Soc.,* **10,** 225-237 (1927).
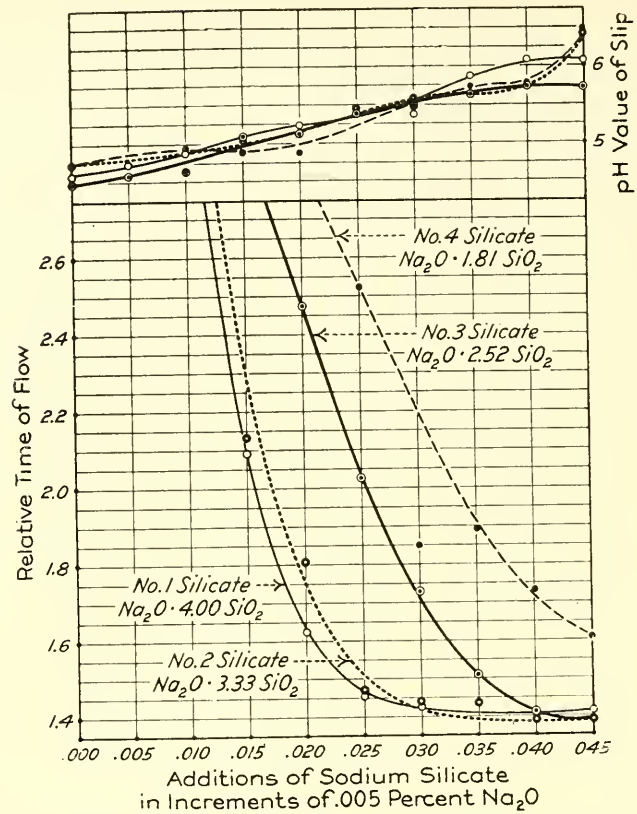
Fig. 141.—Deflocculation of Florida Kaolin with Silicates of Varying Ratio (McDowell).
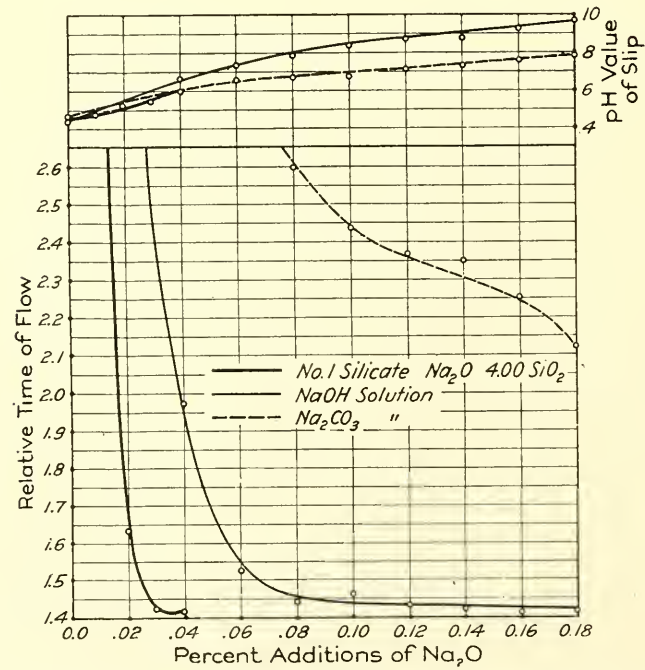
Fig. 142.—Deflocculation of Florida Kaolin (McDowell).

series of clays and measured the hydrogen ion concentration in the slips. The clays behaved differently but it was found that the reduction in time of flow through an orifice was greatest per unit of Na_2O in the mixture when a silicate of ratio 1 : 4 was used.

It is interesting to note that the maximum rate of flow was in each case reached while the slip was on the acid side of neutrality. Comparing the more silicious silicates with sodium carbonate and sodium hydroxide, the silicates were found to have the greatest effect per unit of alkali.

Shop men notice that silicate produces a "stringy slip" compared with sodium carbonate, which yields a slip with high surface tension, if both are brought to minimum viscosity. The former is advantageous in casting clay wares. Silica sol prepared by Bradfield's method had no appreciable effect.[8] It is not a deflocculating agent.

McDowell offers an explanation of the potency of silicate solutions as due to the adsorption of positive sodium ions on colloidal silica. Thus their equilibrium with hydroxyl ions is disturbed and the latter may then become more active in forming hydroxyl ion complexes with positively charged particles and ions and thus reach maximum charge for that system.

Flocculation and Deflocculation by Silicates. Many other finely divided substances are deflocculated by silicate solutions, including most silicious minerals, while many sulfide minerals undergo the reverse and are flocculated.[9] This is a fortunate circumstance, for the condition favorable to the concentration of ores by flotation is to have the valuable minerals in a flocculated condition. By causing the worthless parts of the ore to deflocculate they are kept out of the froth and separated. Silicates of soda are useful reagents to render the gangue particles unfloatable, while the valuable minerals are carried up in the froth from which they are recovered.[10-13]

Flotation. Silicate solutions are particularly useful in flotation circuits in which it is desired to recover two valuable minerals separately. Even relatively high concentrations (0.25 per cent in one instance) deflocculated the gangue without causing either zinc or lead sulfides to

[8] *J. Am. Chem. Soc.*, **44**, 965-74 (1922).
[9] Kohl, H., *Ber. deut. keram. Ges.*, **3**, 64-77 (1922) ; *C. A.*, **16**, 4311.
[10] Weinig, Arthur J., and A. J. Palmer, *Quarterly of the Colorado School of Mines*, **21**, 2 (1926).
[11] Edser, Edwin, 4th Colloid Report, Scientific and Industrial Research, London : His Majesty's Stationery Office (1922), p. 263 *et. seq.*
[12] Edser, Edwin, U. S. Pat. 1,337,548 (April 20, 1920).
[13] Wright, C. A., J. S. Parmelee and J. I. Norton, *Bur. of Mines, Bull.* **205** (1921).

float. It was then possible to deflocculate the zinc blende and float the galena by adding soap, after which dilution was sufficient to cause the zinc blende to be removed separately while the silicate maintained the gangue deflocculated and unfloatable.

The technic of differential flotation is complicated and difficult, but silicates of soda are well recognized as useful controlling agents because of their property of selective deflocculation.[14, 15]

As in clay deflocculation, attention to the time factor is important. Silicates, as Kohlrausch showed, do not quickly reach equilibrium, and will not therefore necessarily give the same results with the same concentration and different times of contact.

The kinds of silicate most suitable for deflocculation appear not to have been investigated in any published work, from the point of view of flotation, but empirical testing has led to large-scale use of Na_2O, $2SiO_2$ and Na_2O, $3.3SiO_2$.

Technic of Application. Borcherdt [16, 17] has elaborated a technic for the application of soluble silicates to certain ores of zinc. The first step is to rid the ore pulp of some of its colloidal constituents by deflocculating and decanting them, a variant of the method already described for refining clay.[18] Na_2O, $3.3SiO_2$ accomplishes this at less cost than other available reagents. The second step is to use silicate solutions for controlling the flotation operation itself. If colloidal gangue minerals are not deflocculated they will contaminate the froth which, aside from impurity, becomes very difficult to handle.

Differential Flotation of Variety of Ores. Silicate is available to induce differential flotation of a great variety of ores, among them not only sulfide ores, but oxidized or non-sulfide minerals and those which have been sulfidized. Copper, lead, zinc, tin, tungsten, molybdenum, silver, antimony, coal, and calcium phosphates have been treated by processes in which soluble silicates serve as deflocculants and control flotation.[19-21]

[14] Fahrenwald, A. W., *Bur. of Mines Report,* 2700 (Aug. 1925).
[15] Minerals Separation, Ltd., Brit. Pat. 154,870 (March 9, 1920) ; *C. A.,* **15,** 1129.
[16] Borcherdt, W. O., U. S. Pats. 1,446,375 (Feb. 20, 1923) ; *C. A.,* **17,** 1415; 1,446,376, 1,446,377, 1,446,378, 1,445,989 (Feb. 20, 1923) ; 1,454,838 (May 8, 1923).
[17] Borcherdt, W. O., Can. Pats. 232,145, 232,148-9, 232,151 (June 19, 1923) ; 233,601 (Aug. 14, 1923) ; *C. A.,* **17,** 3154.
[18] Electro-Osmose A. G., Brit. Pat. 143,920 (1920) ; *C. A.,* **14,** 2908.
[19] Edser, E., and L. A. Wood, Brit. Pat. 168,927 (March 20, 1920) ; *C. A.,* **16,** 405.
[20] Edser, E., H. L. Sulman, and F. B. Jones, Brit. Pat. 159,285 (Nov. 20, 1919) ; *C. A.,* **15,** 2173.
[21] Broadbridge, W., and E. Edser, Brit. Pat. 171,155 (1920) ; *C. A.,* **16,** 985.

The amount used varies greatly with individual cases. Varley reports 0.0951 kilogram per metric ton (0.0863 pound per short ton) of ore treated as average for lead, lead-silver, molybdenum, tin, and miscellaneous in 1920.[22] A mill which uses silicates in both lead and zinc circuits employs 0.498 to 1.494 kilograms per ton (1 to 3 pounds per ton), the upper limit being set by the point at which pyrite begins to be deflocculated and carried into the froth.[23, 24]

Other Uses of Deflocculating Power. It is obvious that deflocculation of useless materials is a help, not only when simple decantation is used, but in other hydraulic means of separation, as wet screening, jigging, or table concentration in which for practical purposes the deflocculated mineral becomes a part of the liquid. Amounts of the order of 1.992 kilograms per ton (4 pounds per ton) of dry ore are effective.[25] Five per cent is the highest figure which has been noted.

High speed mechanical disintegration in the presence of much water, as in the "colloid mill," is fostered by the presence of a colloid of the same sign as the material to be dispersed. Thus, 10 parts of a silicate solution per hundred of zirconium oxide were effective in separating it from the minerals with which it was associated; and phosphates, feldspars, or other raw products are rendered colloidal and available for fertilizers by the same process.[26, 27]

Measuring Detergency by Deflocculation. Fall[28] attacked the problem of measuring detergency by choosing a standard and easily determined material which should be as nearly as possible typical of dirt. A very finely divided manganese dioxide was used and its deflocculation by various detergent solutions studied. Its behavior was ascertained to be similar to that of ferric oxide, clay and lamp black. A series of soaps and alkaline compounds including silicates of soda was considered. A good bibliography was also assembled.

Soaps were found to exert their greatest suspending power in the range 0.2 to 0.4 per cent concentration while caustic soda, sodium carbonate, trisodium phosphate and all the silicates show their greatest ability to peptize solid dirt in the range 0.0125 to 0.05 per cent. The

[22] *Bur. of Mines Serial* No. **2203** (1921).
[23] Marquand, A. B., personal communication; also *Eng. & Min. J. Press,* 5-8, 756-762 (1926).
[24] Morley, Walter S., *Trans. Am. Inst. Mining and Met. Eng.,* No. **1085M** (1921); *C. A.,* **15,** 3436-3437.
[25] Borcherdt, W. O., U. S. Pat. 1,448,514 (March 13, 1923); 1,448,515 (March 13, 1923).
[26] Plauson, L. Ed., Brit. Pat. 196,944 (Oct. 28, 1921); *J. Soc. Chem. Ind.,* **42,** 622A; *C. A.,* **17,** 3672.
[27] Plauson, L. Ed., Brit. Pat. 195,655 (June 28, 1922); *C. A.,* **17,** 3743.
[28] *J. Phys. Chem.,* **31,** 801-849 (1927).

silicates are more like soap in their action than any of the other materials.

The other alkaline salts do not always act as suspending agents and when they do they suffer a decrease as the temperature is raised. Soaps and silicates are also more effective at 40°C. than at 75°C. The most
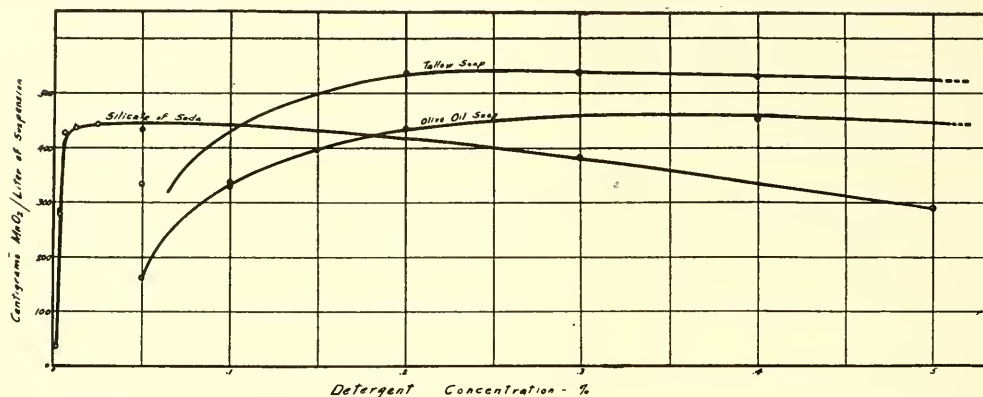
FIG. 143.—Deflocculation of Manganese Dioxide at 40°.

silicious silicate, ratio 1:4, was found to be best at concentrations above 0.15 per cent and at its optimum concentration, 0.025 per cent, was able to suspend substantially the same as olive oil soap at its optimum concentration.

In terms of efficiency per unit of weight the silicate is much more effective, while if the comparison be placed upon units of cost the contrast is still more spectacular.

TABLE 92. *Comparison of the "MnO₂ Values" of Various Compositions of Three Different Silicates of Soda at 40° and at 75°C.*

1 gram portions of MnO_2 ground in a colloid mill (No. 2).
50 cc. portions of silicate of soda solutions.
Values given represent centigrams of MnO_2 present in one liter of suspension as calculated from an analysis of 25 cc. of suspension. These values are the average of duplicate determinations.

Conc. Per Cent	"S" Brand *		"K" Brand ⊕		"BW" Brand †	
	40°	75°	40°	75°	40°	75°
0.5	292	240	219	205	40	61
0.3	382	261	316	247	219	200
0.15	396	287	394	300	396	300
0.05	434	346	430	342	431	344
0.025	445	351	431	342	452	348
0.0125	436	348	433	334	437	313
0.0062	427	216	297	247	404	227
0.0031	278	000	41	000	203	38
0.0015	36	000	000	000	19	000

* "S" Brand is Na_2O, $3.97SiO_2$, specific gravity 1.30.
⊕ "K" Brand is Na_2O, $2.92SiO_2$, specific gravity 1.48.
† "BW" Brand is Na_2O, $1.62SiO_2$, specific gravity 1.68.
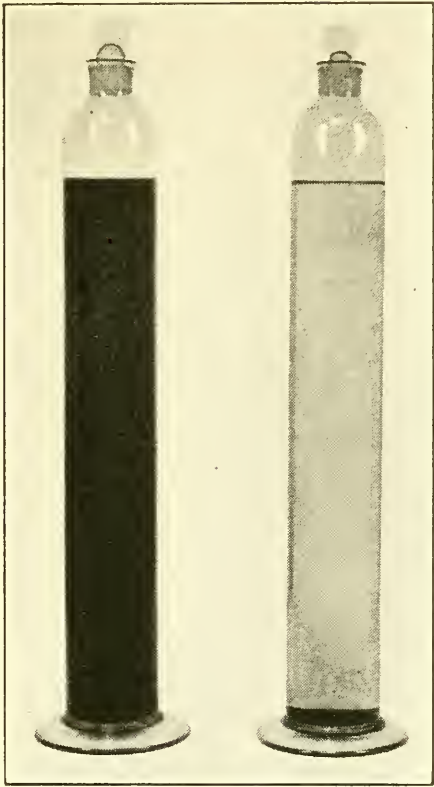
FIG. 144.—Deflocculation of Manganese Dioxide by Silicate.

TABLE 93. *Comparison of the "MnO₂ Values" of Various Concentrations of Five Different Commercial Soaps.*

1 gram portions of MnO_2 ground in a colloid mill (No. 1).
50 cc. portions of soap solutions.
Values given represent centigrams of MnO_2 present in one liter of suspension as calculated from an analysis of 25 cc. of suspension. Values given are the average of triplicate determinations.

At 40°C.

Conc. Per Cent	Olive Oil Soap	Tallow Soap	Palm Oil Soap	Green Arrow Soap	Silicated Green Arrow
2.0	412	327	302	387	278
1.4	440	427	377	435	384
0.8	468	496	420	475	486
0.4	453	532	512	522	505
0.2	435	539	550	520	522
0.1	336	328	335	285	323
0.05	162	334	278	320	360

At 75°C.

Conc. Per Cent	Olive Oil Soap	Tallow Soap	Palm Oil Soap	Green Arrow Soap	Silicated Green Arrow
2.0	322	316	299	325	282
1.4	352	372	342	348	341
0.8	427	433	409	427	416
0.4	433	455	453	448	432
0.2	416	460	455	457	450
0.1	153	322	304	250	261
0.05	85	123	141	134	219

When soap is used at concentrations below the optimum, silicates have more effect in increasing the suspending power of the solutions than other alkaline salts. Also the range of concentrations in which silicates are effective is greater. The effect is also obtainable through a fairly wide range of ratios.

TABLE 94. *Comparison of the "MnO₂ Values" of Various Concentrations of Different Alkaline Solutions at 40°C. and at 75°C.*

1 gram portions of MnO₂ ground in colloid mill (No. 2).
50 cc. portions of alkaline solutions.
Values given represent centigrams of MnO₂ present in one liter of suspension as calculated from an analysis of 25 cc. of suspension. These values are the average of duplicate determinations.

Conc. Per Cent	"S" Silicate* 40°	"S" Silicate* 75°	NaOH 40°	NaOH 75°	Na₂CO₃ 40°	Na₂CO₃ 75°	Na₃PO₄ 40°	Na₃PO₄ 75°
0.5	292	240	000	000	000	000	000	40
0.3	382	261	000	000	000	000	000	140
0.15	396	287	17	52	000	12	70	274
0.05	434	346	232	231	30	99	350	290
0.025	445	351	347	269	110	196	365	291
0.0125	436	348	373	252	284	234	273	248
0.0062	427	216	333	140	203	140	125	113
0.0031	278	000	17	000	68	17	40	000
0.0015	36	000	000	000	000	000	000	000

* "S" Silicate is Na₂O, 3.97SiO₂, specific gravity 1.30.

The similarity between the deflocculating action of silicates and that of soaps is striking. Its bearing on the efficiency of washing processes needs further study, but it is quite evident that large amounts of silicate relative to soap will stably suspend dirt at low cost.

The deflocculating power of silicate solutions has been used to produce a lithopone of extraordinary dispersion and light-resistant quality. Ultramarine is also graded by deflocculating with silicate.[29]

Moses[30] found that small additions of silicate solutions could so disperse the clay substance in a road base that practically all the water was colloidally adsorbed and did not expand when reduced to temperatures below freezing. This meant in practice that a road could be built of earth and yet be free from danger of heaving with frost.

Relation of Deflocculation to Washing Practice. Deflocculation is a vital consideration in washing practice, for a large amount of the ordinary soil of clothing or other materials which we need to cleanse is not soluble in any permissible reagent and must be removed in a state of suspension. Deflocculation makes this possible.[31]

[29] Drefahl, Louis C., and Edward A. Taylor, U. S. Pat. 1,486,077 (Feb. 4, 1924).
[30] Moses, D. V., personal communication.
[31] Fall, P. H., *loc. cit.*

Spring [32] was able to deflocculate a specially purified carbon black, also silica and alumina, with soap so that they would pass without even discoloring a filter paper which completely held them when no soap was present.

Richardson found that a suspension of unusual stability could be made by shaking lamp black containing free fatty acid and hydrocarbon oil with a dilute silicate solution. The same degree of stability could not be secured by shaking lamp black which contained only neutral hydrocarbon oil in a soap solution.[33]

Use of Deflocculation. Deflocculation, then, is the result of specific relations between the substance to be dispersed and the reagent. Silicate solutions deflocculate quartz permanently, i.e., disperse it to a point where Brownian movement overcomes gravity, and sedimentation does not occur.[34] Most silicious minerals are readily dispersed by silicate solutions. These constitute the principal part of dirt which is to be removed by washing. Pyrite, and many other sulfide minerals, are flocculated in silicate solutions, a characteristic which is employed to separate valuable sulfides or sulfidized minerals from silicious gangues. The method has proven very valuable in the treatment of lean ores by flotation.

WETTING POWER.

Conditions Necessary for Wetting. Substances which are deflocculated in aqueous solutions must first be wet, and washing is the release from wet surfaces of contaminating material.[35] Any evidence that silicate solutions cause water to spread in an even film over a surface bears, therefore, upon the problem of their detergency.

Water stands in drops upon an oiled surface but does not wet it. This is also true of many substances which are quite free of oil or grease. Sulman [36] found that the angle between a surface and a liquid which stands upon it is, within certain limits, definite and characteristic. It makes a difference whether a position of equilibrium is attained by means of the liquid spreading over a dry surface or by recession from a surface which has been covered. A drop of water moving down a window pane meets the glass at different angles on the upper and lower

[32] Spring, W., *Rec. Trans. Chim.*, **28**, 120-135, 424-38 (1909) ; **29**, 1-17 (1910) ; *Z. Chem. Ind. Kolloide*, **4**, 161 (1909) ; **6**, 11, 109, 164 (1910).
[33] *Ind. Eng. Chem.*, **15**, 241-3 (1923).
[34] Edser, Edwin, Fourth Colloid Report, Sci. & Ind. Research, London: His Majesty's Stationery Office, **1922**, p. 169.
[35] Traube, I., and K. Nishizawa, *Kolloid Z.*, **32**, 383-392 (1923) ; *C. A.*, **17**, 2982.
[36] *Bull. Inst. Mining & Met.*, **29**, 44 (1920).

sides. Sulman suggested calling the difference between the maximum values the hysteresis of the contact angle. Edser says that alkalies, particularly sodium silicate, reduce both contact angle and the hysteresis. For quartz, both may be reduced to zero. The condition necessary for wetting is the reduction of the contact angle to zero, so silicate solutions wet silicious minerals generally more readily than water is able to do. A simple experiment with almost any kind of textile will indicate that this is also true of animal and vegetable fibers.

These phenomena have to do with the interfacial tension between liquid and solid, which in turn relates to the surface tensions of both liquid and solid. Nuttall [37] says,

"For the liquid to wet, T_2 must be $> T_1 + T_{12}$," where

$T_1 =$ surface tension liquid/air.
$T_2 =$ surface tension solid/air.
$T_{12} =$ surface tension liquid/solid.

Owing to the difficulty of measuring either T_2 or T_{12} there is no proof that this holds in all cases, though it has been demonstrated for some.[38] If this is accepted, it follows that lowering of the liquid/air surface tension will improve wetting power. But the situation is more complicated than this. The surface tension of the surface to be wet has a great influence on the interfacial tension, and disturbing influences such as the concentration of soap or saponin in the surface may work large changes.

Fig. 145.—Experiment Illustrating the Wetting Power of Silicate Solutions.

The wetting power of silicate solutions is illustrated by an experiment suggested by Vincent [39] in which heavy lubricating oil in a six millimeter glass tube is covered with water. The adherence between

[37] Nuttall, W. H., 5th Colloid Report, Scientific and Industrial Research, London: His Majesty's Stationery Office, 28-47 (1923).
[38] Röntgen, A. J., *Wied. Ann. Physik und Chemie,* **2,** 321 (1877).

the oil and the glass is such that the water does not separate them. When, however, a solution of $Na_2O, 3.3SiO_2$ at a concentration of three to four per cent is used instead of the water, it penetrates between the glass surface and the oil, allowing the drop to rise to the surface as illustrated in Figure 145.

Drop Number. The drop number of soap solutions against kerosene is, within limits, a good measure of their wetting power.[40] Applied
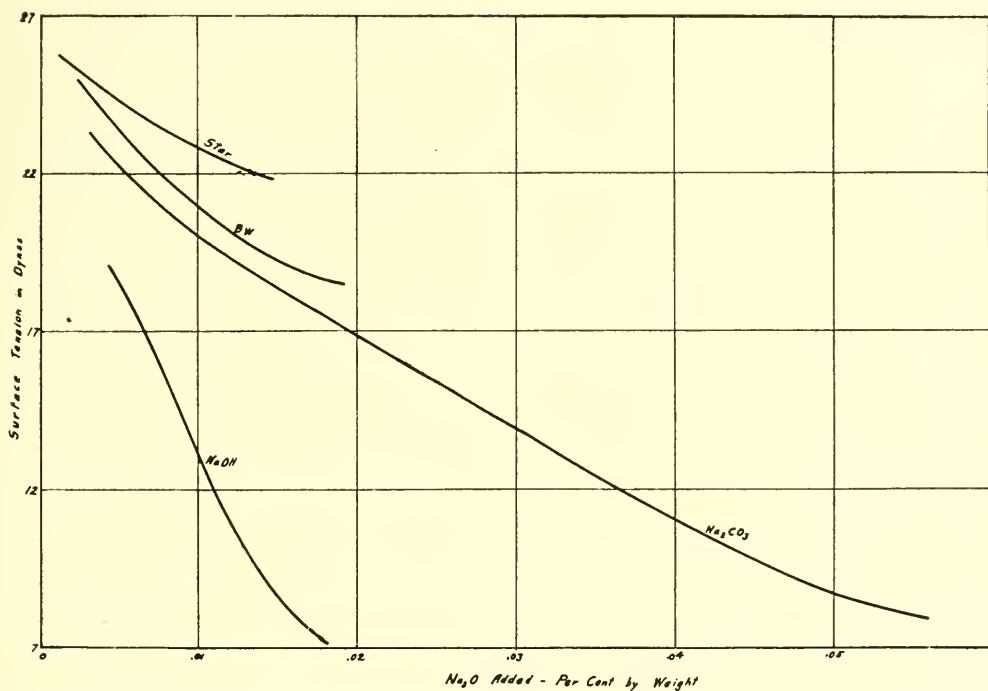
FIG. 146.—Effect of Sodium Carbonate and Silicate on Surface Tension of Soap Solutions at 40°C.

"Star" Silicate is $Na_2O, 2.61SiO_2$, Specific Gravity 1.41.
"BW" Silicate is $Na_2O, 1.62SiO_2$, Specific Gravity 1.68.

to other solutions, the measurement of interfacial tension by this method may be misleading. Soluble silicates when added to water alone do not sensibly affect the drop number against kerosene,[41] yet they do reduce the angle of contact—in some cases to zero. Though they have no appreciable effect on the interfacial tension in the absence of soap,[42] they materially reduce the interfacial tension between soap solution and kerosene.

[39] Vincent, *loc. cit.*
[40] Hillyer, *J. Am. Chem. Soc.*, **25**, 511-532, 1256-1265 (1903).
[41] Richardson, *loc. cit.*
[42] Edser, 4th Colloid Report, Scientific and Industrial Research, London: His Majesty's Stationery Office, **1922**, p. 263, *et seq.*

Millard [43] measured the surface tension of soap solutions with added alkaline compounds against benzene by the drop method at 40°C. Two types of silicate of soda were included. Figure 146 recalculated to show the effect of units of Na_2O in various combinations on surface tension shows that silicates, though less effective than sodium carbonate, have a marked influence.

TABLE 95. *Drop Numbers for Soap Solutions with Added Sodium Silicate at 100°C.*
(Richardson)

Per Cent Soap						
0.25	56	62	..	70	..	91
0.20	44	48	..	55	..	76
0.15	34	39	..	47	..	59
0.10	26	31	..	36	..	45
0.05	18	23	..	27	..	33
0.00	13.5	14	14	14	13.5	13.5
	0.00	0.05	0.10	0.15	0.20	0.25

Per cent Na_2O, $2.83SiO_2$ added

Each of the above drop numbers is the average of two or more tests.

Richardson believes that soluble silicates increase the surface tension of soap solutions toward air, as indicated by decrease of the drop number.[44, 45]

Viscosity and Film Formation. The colloidal character of silicate solutions differentiates them from other alkalies with which they have been grouped. Experience indicates that their effect on surface tension is, like that of gums and gelatin, only a part of the story as far as ability to wet surfaces is concerned.[46] Considerations of viscosity and of film formation were found by Clark and Mann to be of great importance in emulsification, which is closely related to wetting and deflocculation. The colloidal character of silicate solutions gives them viscosities much higher than other alkaline salts and though the available data are meagre, it is well to bear this in mind when considering industrial uses of soluble silicates which depend on wetting power.[47]

Wetting Power and Washing Processes. The value of wetting power has perhaps been too little stressed in discussing washing processes. Any surface which has been completely wet by a detergent liquid has been separated by a film from other substances with which it may have been contaminated. When this condition is attained,

[43] *Ind. Eng. Chem.,* **15**, 810-811 (1923).
[44] Shorter and Ellingworth, *Proc. Roy. Soc. (London), A,* **92**, 231-247 (1916).
[45] Elledge and Isherwood, *J. Ind. Eng. Chem.,* **8**, 793-794 (1916).
[46] Briggs and Schmidt, *J. Phys. Chem.,* **19**, 479 (1915).
[47] Clark, G. L., and W. A. Mann, *J. Biol. Chem.,* **52**, 157-182 (1922).

mechanical processes will do much toward complete removal regardless of the occurrence of deflocculation or the formation of emulsions, helpful though these processes are.

There are several industrial methods which appear to depend primarily upon the ability of silicate solutions to wet surfaces which have been covered with an oily layer.

Recovery of Bituminous Material from Sand. To recover bituminous materials from sands or rock in which they occur naturally it is advantageous to wet the sand with a watery medium, thus allowing separation. This has been done with waters to which various colloidal or alkaline substances have been added. The soluble silicates which combine these two characteristics have served well in a process proposed by Fyleman [48] but developed independently by Clark [49, 50] in connection with the bituminous sands of Alberta.[51] Plant-scale separations have been carried out using an average of 1.518 kilograms (3.25 pounds) Na_2O, $3.9SiO_2$ per ton of sand containing 12 to 17 per cent bitumen, the maximum amount of sand in the concentrate being 11 per cent, the minimum, 5.5 per cent. A temperature of 50° to 90°C. was employed for the silicate treatment. The selection of the most silicious silicate solution to be had commercially was the result of a series of tests, and indicates the value of colloidal characteristics for wetting the sand. Weathered material does not work satisfactorily. The freshness of the sand, the type of treatment with silicate and the mechanical mixing are intimately connected.[52]

Fyleman proposed the use of his process to release oil from sands so far depleted that crude petroleum would not otherwise flow from them. In the laboratory this works out very well but in the field its value depends upon the absence of soluble salts which may react with the silicate and retard the flow.[53] The method is to pump the silicate solution, 0.5 to 2 per cent Na_2O, $3.3SiO_2$, into the lower part of the sand so that the oil may rise above it into an opening from which it can be recovered.[54]

[48] Fyleman, M. E., *Trans. Soc. Chem. Ind.*, **41**, 14 (1922) ; Brit. Pat. 163,519 (1921).

[49] Clark, K. A., 3rd Annual Report, No. 8, Scientific and Industrial Research, Council of Alberta (1922) ; 4th Annual Report, No. 10, 59-73 (1923).

[50] Clark, K. A., and S. M. Blaire, Report Scientific and Industrial Research, Council of Alberta, No. 18, 4-28 (1927).

[51] Egloff, Gustav, and Jacques C. Morrell, *Can. Chem. & Met.*, No. **2**, 33 (1927).

[52] Clark, K. A., personal communication.

[53] *Silicate P's & Q's*, **6**, No. 1 (1926), Philadelphia, Pa.: Philadelphia Quartz Company.

[54] Stroud, Ben K., U. S. Pat. 1,575,944 (March 9, 1926) ; U. S. Pat. 1,575,945 (March 9, 1926).

Purification of Mineral Oils. Mineral oils which have been used for lubricating the crank cases of internal combustion engines, for insulating electrical transformers or for oil-immersion switches become contaminated with finely divided carbon which cannot be removed by filtration. The recovery of these oils will, in the future, assume a greater importance than it has in the past.
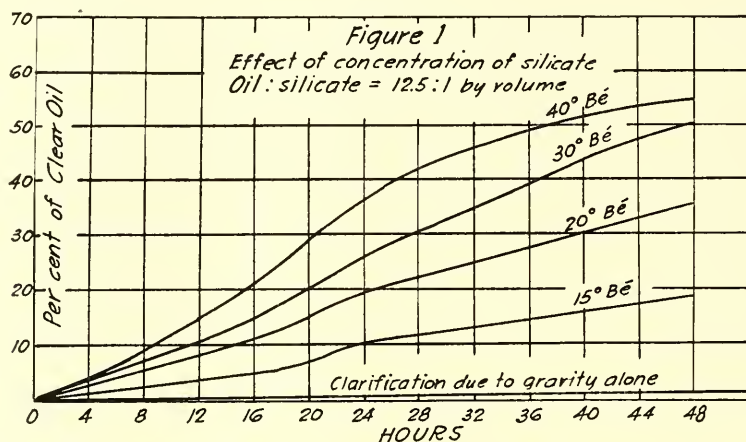
FIG. 147.—Clarification of Mineral Oil by Silicate of Soda (Van Brunt).
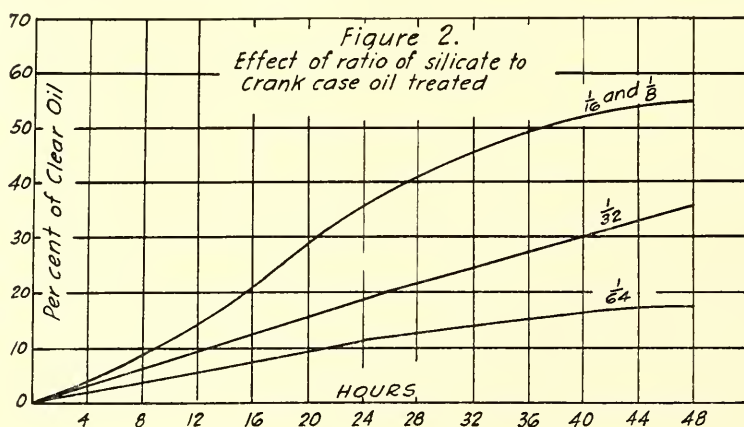
FIG. 148.—(Van Brunt).

Van Brunt and Miller [55, 56] found that by agitating mineral oils containing such colloidally dispersed carbon with a relatively concentrated silicate solution they could cause it to pass completely into the silicate. As the silicate solution is much heavier than the oil it is a simple matter to throw the oil upon a body of water and allow the silicate droplets as they quickly settle out to carry the carbon past the interface into

[55] Van Brunt, C., and Miller, P. S., *Ind. Eng. Chem.*, **17**, 418 (1925).
[56] Van Brunt, C., *Ind. Eng. Chem.*, **17**, 966-7 (1925).

the aqueous layer, leaving the oil free of suspended matter. It then remains only to remove the light fractions by heat to obtain an oil ready for re-use. They worked with oils from the crank case of internal combustion engines.

Na_2O, $3.3SiO_2$ at various concentrations yielded a sludge which separated slowly from the oil at room temperatures, as indicated by Figure 149. It is evident that higher concentrations are more effective. Fol-
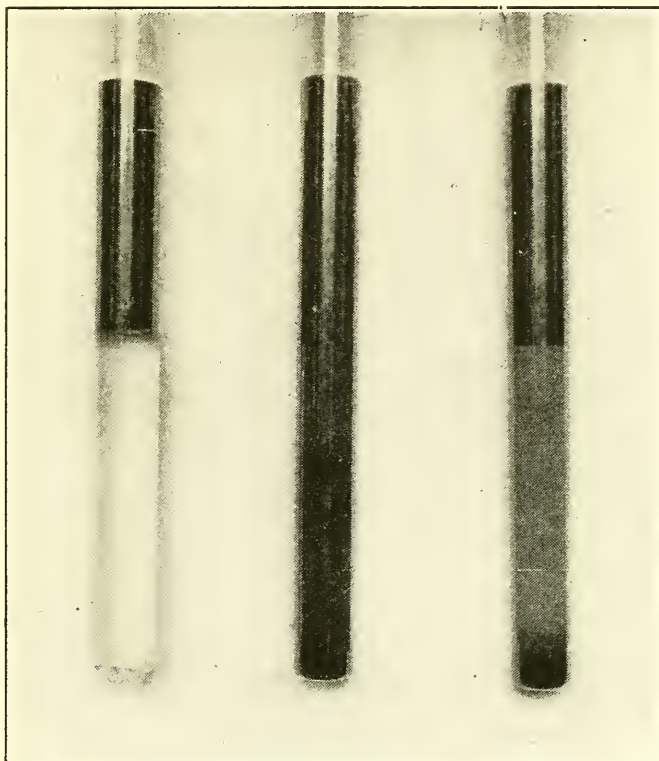
Fig. 149.—Reclamation of Crank Case Oil.

Left hand tube—Oil poured on water. Center tube—After the silicate and suspended materials have dropped out of the oil and passed into the water layer. Right—Same after settling.

lowing this suggestion, Na_2O, $3.3SiO_2$ specific gravity 1.38, was tried in various amounts. Relations between silicate and oil by volume indicate that there is nothing gained by using more than 1 : 16 for sedimentation at ordinary temperatures. Raising the temperature to 80°C. brought the whole clarification of a 5 cm. layer of oil lying on water within 5-6 minutes and amounts of silicate solution down to 1 per cent were found to be sufficient for some oils.

Contaminated crank-case oils are not simple suspensions of carbon in hydrocarbon liquids, and some were found which did not yield to
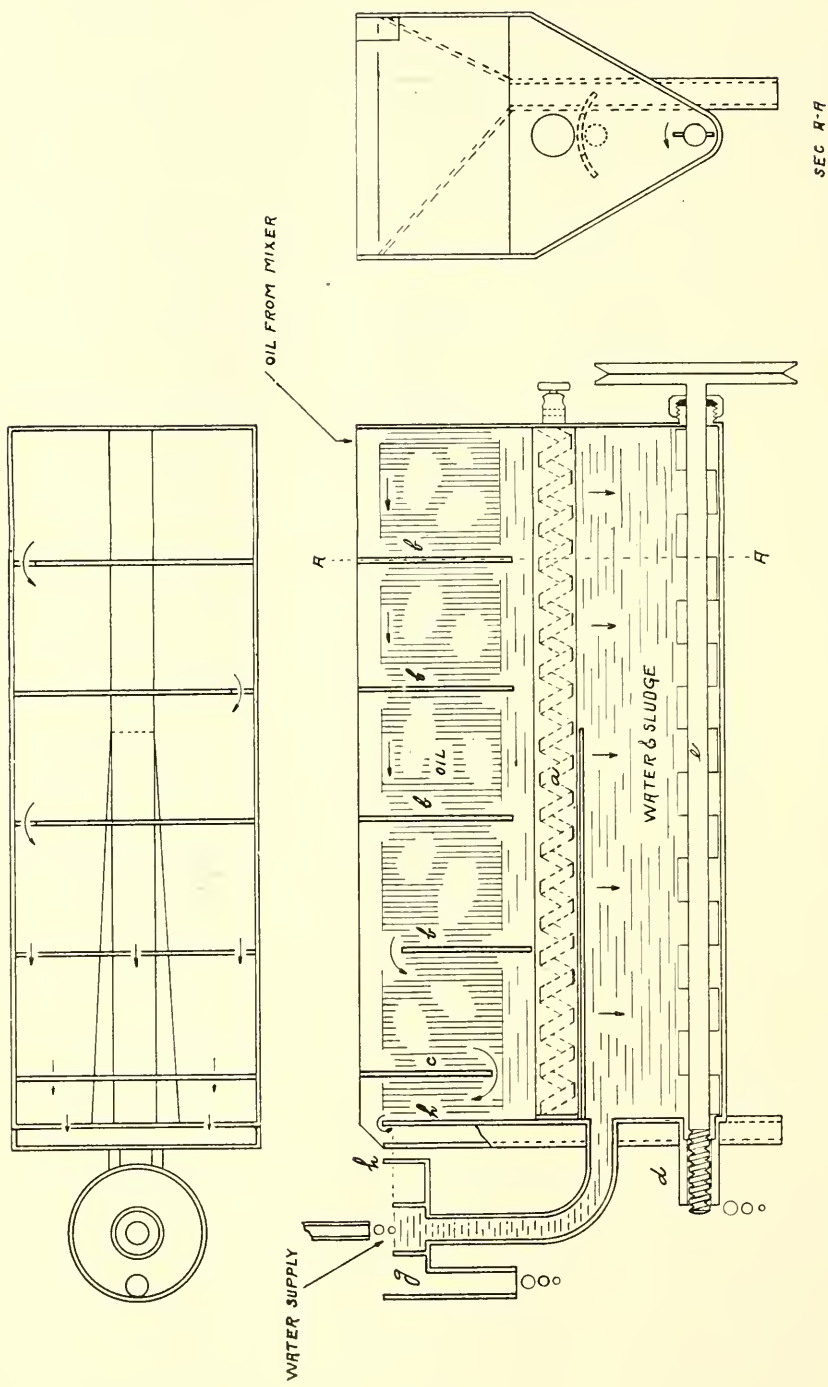
FIG. 150.—Diagram of Clarifier Used for Continuous Reclamation of Contaminated Automobile Crank Case Oil (Van Brunt).

this treatment, either by failing to clarify or by producing a sludge which was not easily dispersed by water. All these were brought into line by adding a mixture of acid manganese resinate and stearic acid in the proportion of 1 : 200 and 1 : 1000 respectively, followed by a 1 : 40 by volume addition of $Na_2O, 3.3SiO_2$, specific gravity 1.38. A single exception was an excessively dirty sample which required twice the amount of silicate.

Better dispersion of the sludges and hence easier operation of mechanical devices was secured by using a still more concentrated silicate,—$Na_2O, 1.6SiO_2$, specific gravity 1.67.

The method of agitation found to be most satisfactory is to break up the silicate into small droplets, just enough to give complete contact, but not enough to form an emulsion which may occur if too much agitation is used in a relatively clean oil. This can be prevented by adding carbon black. Air was also found to be essential and must be broken into fine bubbles during the period of agitation. The authors comment that this is undoubtedly connected with the fact that not only the more polar bodies in the oil but also the silicate tend to enter the oil-air interface. They promise a theoretical discussion of the action of the silicate solution from the point of view of colloid chemistry.

This should be of great interest. The observation may, however, be made that the process seems to be essentially a wetting of carbon, colloidally dispersed in the oil, by a silicate-soap solution heavy enough to settle rapidly from the oil and soluble enough to be easily dispersed in water.

The presence of resin or oleic acid would guarantee the formation at least of traces of soap and acidic materials; manganese or other metallic salts would cause a precipitate in the concentrated silicate which might, like the carbon black, favor the separation. This, of course, is not a complete description of the observed phenomena, but the process affords a striking example of the ability of silicate solutions to wet surfaces which completely repel water, as well as their part in suspending carbon after bringing it into water. Soap solutions and other alkaline salts were tried and found greatly inferior to the silicates.

Other workers have used silicate solutions to wet colloidal carbon and removed the sludge with the aid of centrifugal apparatus. While oils of satisfactory quality may thus be produced it is neither so convenient nor economical to completely free the sludge from oil as in the Van Brunt method.[57]

[57] Rhodes, F. H., and H. J. Haon, *Ind. Eng. Chem.*, **17**, 25 (1925) ; cf. Flowers, A. E., F. N. McBerty, and R. Reamer, *Ind. Eng. Chem.*, **17**, 481-485 (1925).

Clark [58] is of the opinion that positive charges on the colloidal carbon have to do with the ease with which the silicate solution wets it. The result of his centrifugal process is said to yield from contaminated switch oil a product of superior resistance to emulsification, reduced acidity, and a dielectric strength comparable to new oil. The carbon from arcing switches under oil and from burning motor fuel in an engine cylinder appears to be equally amenable to wetting by silicate solutions.

Silicate solutions have been used in mineral oil refining to remove traces of acid from lubricating stocks. As the relatively concentrated solutions employed are heavier than other neutralizing agents they can be quickly and completely settled from the oil at a saving of time. In some cases the operation has been carried out in a few hours at low temperatures such that a sodium carbonate solution would remain suspended for weeks. [59]

Vegetable Oil Refining. Vegetable oil refining also employs silicate solutions either alone or in connection with the well known method of refining with caustic soda. Procedures vary according to the nature of the particular oil, but in each case the alkali causes the separation of a flocculent precipitate containing soap and much of the coloring matter of the oil. Silicate solutions are able to wet this soap without forming troublesome emulsions, if appropriate conditions are observed, and a denser residue with consequent higher recovery of oil is obtained due to the weight imparted by the silicate.

Two methods are recommended for linseed oil,—one employing Na_2O, $3.3SiO_2$ and NaOH, the other using Na_2O, $1.6SiO_2$ alone. The first uses 0.15 pound per gallon of a mixture consisting of 3 volumes of 1.79 specific gravity (22° Baumé) NaOH and 1 volume of 22° Baumé Na_2O, $3.3SiO_2$, for each per cent of free fatty acid in the oil. [60] This mixture is emulsified by stirring at atmospheric temperature, and then slowly heated until a flocculent precipitate separates—in the language of the trade, till it "breaks." The soap and silicate settle rapidly, and the oil is decanted, washed to free it from traces of soap, treated with fullers' earth and filtered, giving a light colored sparkling oil.

The second method requires 0.1 pound of Na_2O, $1.6SiO_2$, 1.67 specific gravity (58° Baumé), for each per cent free fatty acid and heating to not more than 70° C. Otherwise the procedure is the same as above.

[58] Clark, L. H., personal communication.
[59] Michler, J. R., *Chem. Ztg.*, **21**, 853; *J. Soc. Chem. Ind.*, **16**, 1009 (1897); Otto, O. T., Brit. Pat. 158,252 (Jan. 17, 1921); *C. A.*, **15**, 1954.
[60] Hartman, F. E., "The Truth about Ozone," Scottdale, Pa.: U. S. Ozone Co., **1922**.

Soft water should be used in washing the oil, as calcium compounds tend to cause emulsions that are hard to break.

Cottonseed oil is the most important subject of this refining method though it is applicable to peanut oil and most of the liquid fats. The technic must be varied according to the quality of the raw oil. In wet seasons the seed often heats before the oil is pressed from it and enzyme action increases the content of free fatty acid. Such oils produce a large precipitate in refining and consequent loss which may be reduced by the use of silicate. The art of the refiner consists in knowing how much alkali to add and at what concentration, the time of agitation before heating, and the temperature to use in breaking the emulsion. All these must be adjusted to the quality of the crude oil because they affect the color, flavor, and value of the final product. A large mill working by the silicate process obtained an increase of 1.7 per cent yield on prime crude cottonseed, and the advantage is much greater when high free acid or abnormal color has to be dealt with.[61]

Variations of the general method including the use of sodium carbonate and different sequences of the steps have been patented, but essentially it depends upon the wetting and weighting of the flocculated albuminous and other impurities by silicate solutions which form a dense soap stock and increase the recovery of oil suitable for an article of diet and commanding a corresponding price. The practice is well established and has for years been used on a large scale.[62, 63]

Purification of Fats and Fatty Oils. Fats and fatty oils may also be purified by treating their solutions in ether, benzene, or other volatile solvents with silicate solutions. A compact dry soap settles out quickly and the solvent is recovered by distillation. $Na_2O, 3.3SiO_2$ at 1.38 specific gravity is recommended.[64, 65]

Solvents such as those used by dry cleaning establishments are also amenable to purification by agitation with silicate solutions which settle readily.[66]

Anti-Dimming Compounds. Compounds designed to cause the spread of rain drops in an even film upon glass frequently contain soluble silicates. Such compounds are important means of improving vision through the windshield of an automobile or through glass pro-

[61] *The Balance,* **2,** 3 (1925), Fort Worth, Texas: Fort Worth Laboratories.
[62] Chisholm, Jesse C., U. S. Pats. 1,007,642 (Aug. 31, 1911) ; 1,056,261, 1,056,262, 1,056,263, 1,056,264 (March 18, 1913).
[63] Holbrook, George M., U. S. Pats. 1,169,154, 1,169,155 (Jan. 25, 1916).
[64] Salmonson, H. W., Brit. Pat. 13,970; Brit. Pat. 165,635 (May 20, 1920) ; *C. A.,* **16,** 847.
[65] Telenga, Jan., *N. Y. J. of Commerce* (Jan. 28, 1922).
[66] Hey, H., Brit. Pat. 164,931 (April 27, 1920) ; *C. A.,* **16,** 600.

tectors for marine or other observers. They also serve to prevent fog on mirrors used for dental work.[67]

They were used also in connection with gas masks during the war, more than 9 million units of a compound in the form of sticks having been delivered to the American armies before the signing of the armistice. The formula used for this purpose was:

> 100 parts 85 per cent turkey red oil,
> 15 parts NaOH or equivalent Na_2CO_3,
> 5 parts paraffin oil,
> 5 parts $Na_2O, 3.3SiO_2$, specific gravity 1.38.

The composition may be varied as set forth in patents [68] dedicated to free use by any person in the United States.

Sulfonated rape-seed or cottonseed oils may be used and water in varying amount to make a consistency suitable for saturating cloth, for paste, or sticks similar to those in vogue for shaving soap.

Variations of this idea are possible without losing the effect of the silicates. Ridgeley [69] had good results from a mixture of soap, glycerin, and silicate.

Differential Wetting of Valuable Minerals. Differential wetting of valuable minerals, notably gold and platinum-bearing sands, is secured by flowing the ore pulps against a surface prepared with a mixture of petroleum grease, animal oil or fat, and silicate of soda. The ores are said to adhere while the gangue materials do not.[70]

EMULSIFICATION.

Types of Emulsions. The interfacial tension between silicate solutions and oils is very low. This favors wetting and the formation of emulsions, of which there are two types, oil in water and water in oil. The emulsions formed in detergent operations are of the type in which water is the continuous phase, while oil is the continuous phase in emulsions in which crude petroleum comes from the earth, bearing large amounts of water.[71, 72]

Great stress has been laid upon the importance of emulsifying oils and fats as one of the fundamentals of washing. It has already been indicated that such materials can be separated from surfaces to which

[67] Carleton, P. W., *Ind. Eng. Chem.*, **21**, 1105-1111 (1919).
[68] Kuhn, H. A., U. S. Pats. 1,394,773, 1,394,774 (Oct. 25, 1921).
[69] U. S. Pat. 1,556,714 (Oct. 13, 1925).
[70] Luckenbach, Roger, U. S. Pat. 1,478,237 (Dec. 18, 1923).
[71] Clayton, W., "Theory of Emulsions and Emulsifications." London: Churchill, **1923.**
[72] Bancroft, Wilder D., "Applied Colloid Chem.," Chap. IV, New York City: McGraw-Hill Company, **1921.**

they have been attached by interposing an aqueous film without necessarily making an emulsion.[73]

Emulsifying Power of Silicates. Hillyer[74] stated that sodium silicate would not emulsify cottonseed oil which had been treated with dilute sodium hydroxide to remove free fatty acid, but he specified neither the composition nor concentration of the silicate, a frequent error of those who are not familiar with the variety of substances which is included in the term silicates of soda.[75]

Stericker's[76] experiments show plainly that emulsions can be formed with silicate solutions in any but the most refined grades of mineral oil and that in the case of the more silicious silicates results can be secured which are not at all in accord with those which would be expected from a consideration of the drop numbers. This method gives results which run fairly parallel to the emulsifying power and detergency of soaps, but are quite misleading when applied to silicates. Richardson's and Millard's[77] drop numbers already cited, would lead to the assumption that sodium carbonate is a more efficient emulsifying agent than any silicate, but Stericker found that emulsifying power in silicates toward mineral oils increases with decreasing alkalinity and that $Na_2O, 3.9SiO_2$ is more effective than sodium carbonate. Pure hydrocarbon oils are but slightly emulsified by silicate solutions and the emulsions are unstable. Kerosene is more readily emulsified than a U.S.P. petroleum for medicinal use. A colored fraction from California crudes, 0.87 specific gravity, is still more readily emulsified. The presence of unsaturated hydrocarbons may account for the difference. Saponifiable oils are readily emulsified by silicate solutions and since they are more effective than sodium carbonate it is evidently not wholly a matter of soap formation. The addition of a small amount of saponifiable oil to the purest mineral oil causes it to emulsify with silicate.

The purified oil yielded two kinds of emulsions, but both were unstable. The optimum conditions for water in oil were 70-90 per cent and a 5 per cent solution of $Na_2O, 3.3SiO_2$, shaken at 20° or 80°C. Small amounts of oil in water were obtained with 2 to 4 per cent of oil and 0.5 per cent solution of $Na_2O, 3.3SiO_2$ or $Na_2O, 3.9SiO_2$.

[73] Mees, R. T. A., *Z. Deut. Öl und Fett Ind.*, **42**, 235-237 (1922); *Chem. Weekblad*, **19**, 825 (1922); *C. A.*, **16**, 2422; BJ, 302-304 (1923); *C. A.*, **17**, 2514.
[74] *J. Am. Chem. Soc.*, **25**, 511 (1903).
[75] Stericker, William, *Ind. Eng. Chem.*, **12**, 1026 (1920).
[76] *Ind. Eng. Chem.*, **15**, 244 (1923).
[77] Richardson, A. S., *Ind. Eng. Chem.*, **15**, 24-3 (1923); Millard, E. B., *Ind. Eng. Chem.*, **15**, 810-811 (1923); Briggs and Schmidt, *J. Phys. Chem.*, **19**, 479 (1915).

The mineral oils which were less refined gave emulsions which creamed out, as did those made by Pickering [78] with soap. All the silicates had some emulsifying power, but under optimum conditions practically all the separated layer could be diluted with silicate solution or with water, showing that the oil was still dispersed and, like defloculated solids, in condition to be rinsed away. Some of these emulsions made with lubricating oil remained emulsified at atmospheric temperature for a month without much separation. In this case, Na_2O, $3.9SiO_2$ at 0.6 per cent and Na_2O, $3.3SiO_2$ or carbonate at 0.4 per cent were best.

With all but the purest oils the best emulsions with silicate-soap mixtures were better than could be made with soap alone.

The emulsifying powers of silicate solutions are considered by Vincent [79] to be due to soaps formed from fatty acids in the oils which silicate has been observed to emulsify. Most dirt encountered in practical washing contains some saponifiable material so that oils are emulsified by silicate detergents even in the absence of soap. He points out, however, that while emulsification is a helpful adjunct to washing, it is not essential as oils may be removed from surfaces from which they are released by the wetting action of detergents even though they are not fully dispersed as emulsions. If the silicate solution is able to squeeze in between the junction of oil and fabric or skin, that is, to wet the surface to be cleaned and displace the oil, then the oil may be removed by rinsing regardless of its degree of dispersion; and this is known to occur.

The action may also be viewed as the detergent wetting the oil and solutions able to wet oily surfaces are seen to have detergent value. In one sense wetting and emulsification are different only in degree,—an emulsified oil may be considered as superlatively wet.

The optimum concentration of soap for forming emulsions for detergent purposes lies in the range 0.05 to 0.1 per cent, while defloculation by soap is most effective at 0.2 per cent to 0.4. Vincent says:

"If a particular soap bar were composed of 80 per cent sodium silicate, $(Na_2O)_2,(SiO_2)_3$ and 20 per cent soap, and if this detergent were used at a concentration of 0.3 per cent, the actual soap concentration would be $0.3 \times 0.2 = 0.06$ per cent. This is within the concentration of 0.05–0.10 per cent necessary to emulsify oils.

"The silicate concentration in the detergent solution would be $0.3 \times 0.80 = 0.24$ per cent. The MnO_2 value of "S" Brand silicate (Na_2O, $3.97SiO_2$, specific gravity 1.30), $(Na_2O)_2,(SiO_2)_{3.97}$, at 40°C.

[78] J. Chem. Soc., **91**, 2001 (1907).
[79] J. Phys. Chem., **31**, 1296 (1927).

is approximately 390. Whereas, the MnO_2 value of the soaps studied exclusive of olive oil soap, at 0.24 per cent and 40°C. is approximately 520.

"This means that the silicate would suspend 390/520 = 75 per cent of the solid material that pure palm oil, tallow, Green Arrow, or silicated Green Arrow soap would suspend.

"At the above concentration and temperature olive oil soap exhibits an MnO_2 value of about 445. Thus, the silicate would be 390/445 = 87.5 per cent as efficient as pure olive oil soap in the suspension of solids.

"By making a bar of soap which contains 20 per cent soap and 80 per cent sodium silicate, the soap would cleanse the liquid dirts, and the silicate would suspend the solids 75-90 per cent as efficiently as would pure soap alone. In reality this percentage would be higher, due to the fact that the soap, as well as the silicate, would suspend the solids to a certain extent.

"The emulsifying powers of such a silicated soap were investigated and found to be excellent."

Concentration and Alkalinity of Silicate Solution. The concentration of silicate solutions is an important factor in forming emulsions. Those which stand heating to 80°C. are best made with silicates of 5 per cent or lower concentrations, while those which can be depended on to break at 70° to 80°C., as in the oil refining processes, are more concentrated. This is fortunate, as the lower concentrations are those appropriate to washing. One of the best emulsifiers consisted of 0.3 per cent neutral soap plus 0.1 or 0.2 per cent $Na_2O, 3.3SiO_2$. The soap-silicate mixtures proved in all cases to emulsify better than soap alone.

The evidence seems conclusive that from the point of view of dispersing oils and fats, silicate solutions rightly chosen and applied are effective alone, and when mixed with soap they perform this part of the detergent process better than a pure soap can do.

What the factors are which determine the concentration, relative alkalinity, and temperature at which silicate will emulsify or cause the coalescence of dispersed oil or water do not appear to be fully known, but experimental evidence and experience in industry show that both can be done. Barnickel [80] has studied the breaking of petroleum emulsions in which oil is the continuous phase. From the foregoing, it might be supposed that a highly alkaline and relatively concentrated silicate would be best.[81] Since calcium and magnesium tend to induce water in oil emulsions, and sodium soaps, the oil in water type, it follows

[80] Barnickel, William, U. S. Pat. 1,093,098 (April 14, 1914).
[81] Bhatnazar, S. S., *Report Faraday and Physics Soc.*, 27-31 (1921).

that water-softening agents help to break the natural petroleum emulsions.[82-87]

LATHERING.

Formation of Foam. Aeration of liquids and the formation of froths and foams take place under the most diverse conditions. Edser [88]
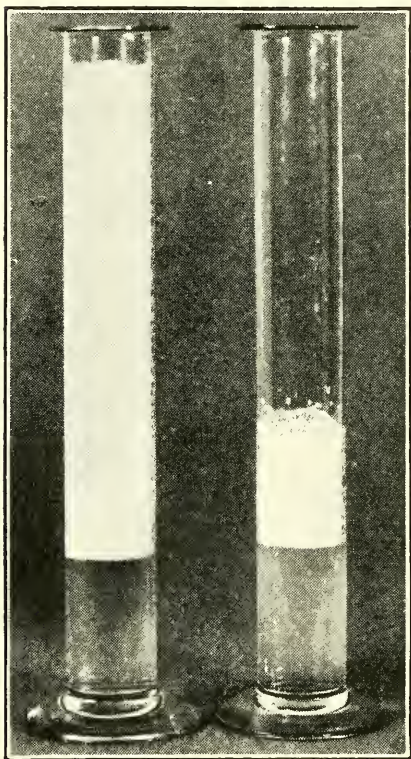
FIG. 151.—Effect of Silicate on Lathering.

The tubes contain the same amount of soap solution. The one on the left contains silicate; that on the right does not.

concludes that the only condition common to frothing liquids is that their surface tension is not normal. It may be reduced, as in the case of soap solutions or the slightly soluble oils used in flotation, or slightly increased, as in the case of electrolytes, among them silicates of soda. Pure liquids do not foam. The stability of foams may be greatly increased by concentration of such substances as soap, saponin, insoluble solids, or liquids in the films.[89] These change the films, in some cases at least, to plastic solids.[90] Thus the materials removed in washing tend to stabilize soap lathers.

Effect of Silicate on Lathering. Silicate solutions alone cause foam, but it is evanescent. They do not concentrate in the surface films as saponin and soap do, but they are able to increase and to stabilize foams produced by soap. Clay and silica added to 0.2 per cent Na_2O, $3.3SiO_2$ solution produced a good suds.[91] Mineral oils also stabilize the foam produced by silicate solutions.

[82] Clowes, *J. Phys. Chem.*, **29**, 407 (1916).
[83] Barnickel, Wm. S., U. S. Pats. 1,223,659 and 1,223,660 (April 24, 1917).
[84] Mathews, R. R., and P. A. Crosby, *J. Ind. Eng. Chem.*, **13**, 1015 (1921).
[85] Donnan, F. A., *Report, Faraday and Physics Soc.*, 18-21 (1921).
[86] Parsons, L. W., *J. Ind. Eng. Chem.*, **14**, 797-798 (1922).
[87] Dodd, H. V., *Chem. Met. Eng.*, **28**, 249-253 (1925).
[88] Fourth Colloid Report, Sci. & Ind. Research, London: His Majesty's Stationery Office, 314-320 (1922).
[89] Freundlich, *Kapillarchemie*, 302 (1909).
[90] Wilson, R. E., and E. D. Ries, Colloid Symposium Monograph, 1, 145 (1923); presented in preliminary form at A. C. S. meeting, Rochester, N. Y. (April, 1921).
[91] Stericker, *loc. cit.*

There is some disparity in the literature respecting the effect of silicates upon the lathering power of soap. This is doubtless due to different silicates and conditions chosen for experiments.[92]

Figures 151, 152 and 153 show experiments in which soap alone and soap with silicate were put into freshly boiled distilled water and
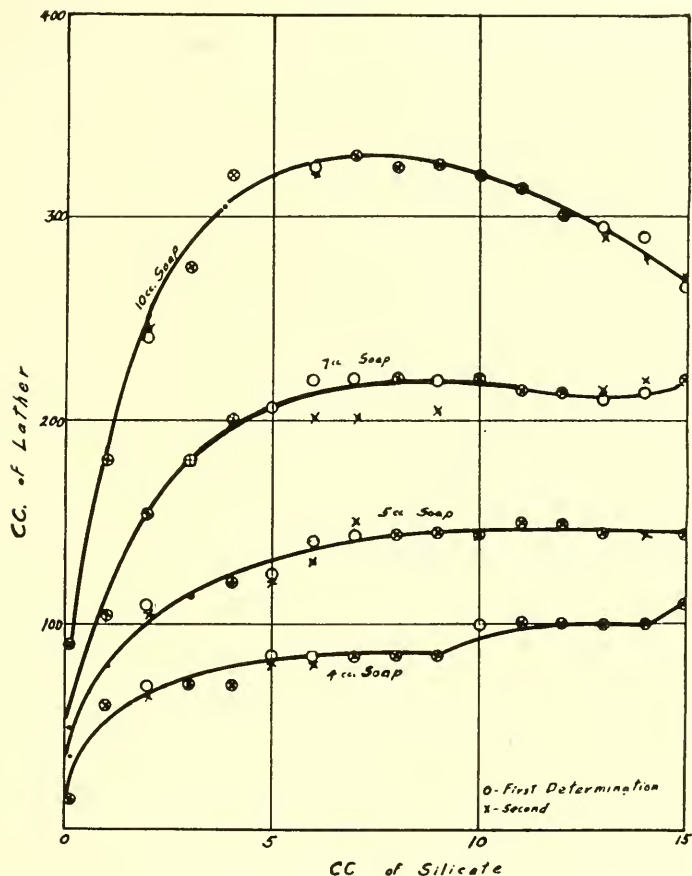
Fig. 152.—Effect of $Na_2O, 3.34SiO_2$, 1.01 Specific Gravity (2°Baumé) Silicate on Volume of Lather.

shaken alike. A 0.5 per cent solution of a high-grade flake soap, well known on the market, was used.[93]

Lathering Power and Detergency. Under optimum conditions silicate is a more effective promoter of lathering in soap than is sodium carbonate.

If an amount of oleic acid soap just below that required to make a

[92] Rasser, E. O., *Seifensieder Ztg.*, **48**, 290, 309, 355, 368 (1921) ; *Textilberichte,* **4**, 277-84 (1923).
[93] *"Silicate P's & Q's,* **6**, *No.* v (1926), Philadelphia, Pa.: Philadelphia Quartz Co.

lather in distilled water be chosen, an addition of sodium carbonate
will enable the liquid to foam when shaken. When the same amount of
alkali is added as silicate the foam is more voluminous and much more
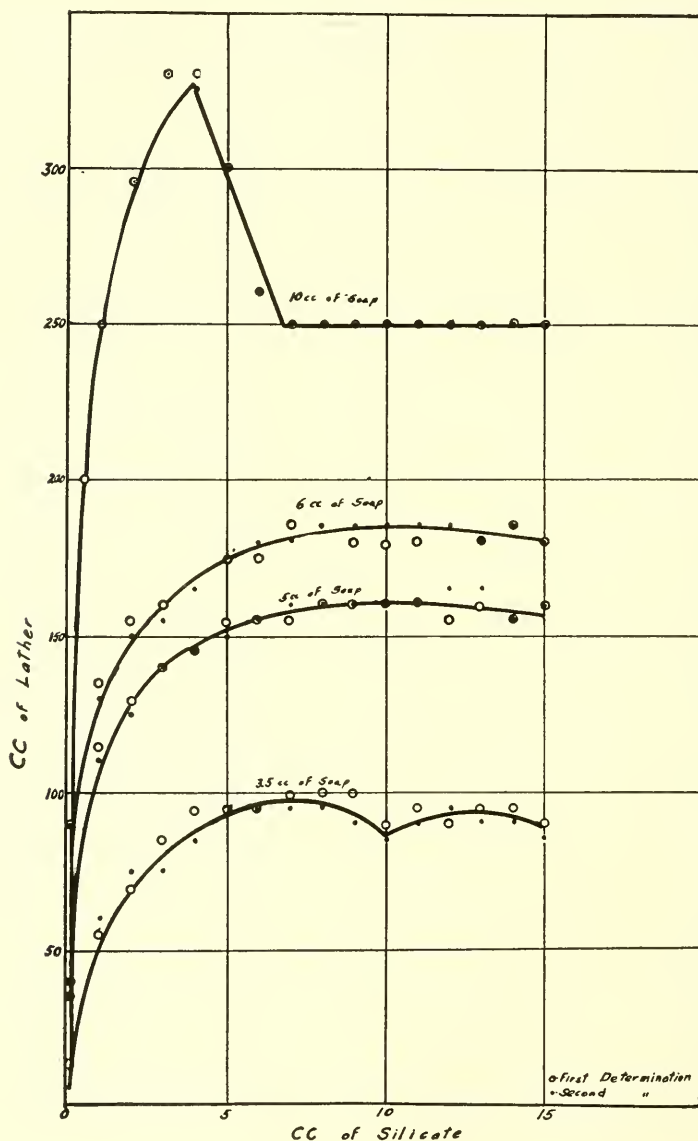
FIG. 153.—Effect of Na_2O, $3.34SiO_2$, 1.04 Specific Gravity (6°Baumé) Silicate on
Volume of Lather in 100 cc. Distilled Water.

stable. As shown in Figure 154, the original turbidity declines with the
addition of soda ash, but the substitution of silicate for carbonate yields
an entirely clear solution under the lather.

Lathering power has been proposed as a measure of detergency.[94]

[94] Chapin, Robert M., *Ind. Eng. Chem.*, 17, 461-465, 1187-1191 (1925).

It is quite obvious that some materials detached from fabrics in washing are carried away in the suds. This is a useful property, and soaps which lather well are usually good detergents, but the value of lather as an index of detergency has a place in the public mind out of proportion to its worth. Foams have good wetting power because the outside surfaces of the bubbles have higher surface tension than the inside, so that they tend to flatten out against a surface of contact.[95]

The permanence of soap lathers has to do with the viscosity of the films and the thickness of bubble walls. Silicates evidently stabilize soap lathers, but the mechanism of the process has not been investigated. Silicates may cause an increase in the surface concentration of the soap.[95, 96]
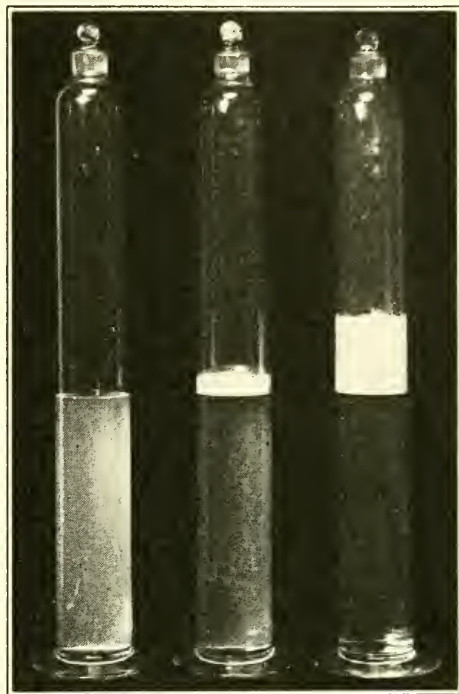
Fig. 154.—Effect of Silicate of Soda on Soap Suds.

First tube .055 g. Na oleate 1000 cc. distilled H_2O.
Second tube .055 g. Na oleate 1000 cc. distilled H_2O. .015 g. Na_2CO_3 equivalent to .008 g. Na_2O.
Third tube .055 g. Na oleate 1000 cc. distilled H_2O. .03 g. Na_2O, $3.25SiO_2$ equivalent to .007 g. Na_2O.

LUBRICATION.

Silicate solutions in common with soap and other alkaline materials have a slippery feel when rubbed between the fingers. It seems probable that this characteristic may have a helpful influence in freeing dirt from a state of entanglement in the fibers of goods as they are moved about in washing.[98]

If there were formed upon the surface of either fabric or foreign material a film such as those described in the following chapter, it would at first assume a soft gelatinous condition. Gelatinous films are very slippery and yield under moderate pressure with a lubricating effect. It seems likely that such films are formed, for small amounts

[95] Shorter, S. A., *J. Soc. Dyers Colorists,* **34,** 136-138 (1918).
[96] Leimdörfer, *J. Chem. Umschau,* **30,** 149-151, 157-161 (1923).
[97] Rasser, E. O., *Seifensieder Ztg.,* **48,** 268-269, 290-291, 309-310, 355-357 (1921) ; *C. A.,* **15,** 2992.
[98] Lamborn, L. L., "Modern Soaps, Candles, and Glycerin," New York: Van Nostrand, p. 21-32, **1906.**

of silicious ash accumulate in all fabrics washed in silicate solutions. From our knowledge of their behavior, we may assume that the silica which forms the ash was highly hydrous when laid down. There are no data as to the extent to which lubrication plays a part in detergency, but it is a factor which must be studied before our knowledge is complete.

SOLUTION.

Solvent Effect of Soap Solutions. The solvent effect of soap solutions was investigated by Pickering,[99] who found that they would dissolve appreciable amounts of benzene and hydrocarbon oils. Silicate solutions do not do this, but the action of soap is not prevented by the presence of silicates. The best naphtha soaps which contain petroleum hydrocarbons to the extent of 10 per cent or more have at least an equal amount of silicate and go into solution without separation of the mineral oil. It is also usual for soap makers to add small amounts of mineral oils along with the silicate in the final mixing of laundry soaps to smooth the texture, and this oil does not reappear as the soap is dissolved for use.

Fatty Acids Saponified by Silicates. The presence of silicates may also hinder the precipitation of calcium soaps from hard water. Silicates are, besides, able to saponify fatty acids which go into solution and these, as we have seen, have a marked effect upon emulsifying and deflocculating power.[100] This is particularly important because small amounts of fatty acid are present as part of the soil in many kinds of washing.

Starches Hydrolized by Silicates. Starches may be hydrolized and brought into solution by the alkalinity of silicates. Starched goods are notably easier to wash clean because when the starch is dissolved in washing, the support of the foreign substances is taken away and they are free to float.[101]

Albuminous materials are dissolved by silicate solutions as by other alkaline reagents.

Solvent Action of Silicates in Straw Paper Industry. The solvent action of silicate solutions upon the non-cellulose constituents of straw has been employed experimentally,[102] though with quantities of several tons, for reducing wheat straw to pulp for making the straw

[99] Pickering, S. V., *J. Chem. Soc.,* 111, 86-101 (1917).
[100] Shorter, S. A., *J. Soc. Dyers Colourists,* 36, 299-304 (1920) ; *C. A.,* 15, 1222.
[101] de Keghel, M., *Rev. chim. ind.,* 30, 171-178 (1921) ; *C. A.,* 16, 1020.
[102] Dixon, U. S. Pat. 52,545 (1866) ; Cobley, T. H., Brit. Pat. 13,096 (1896).

paper used in the container industry. The method has the advantage, over the usual treatment, of freedom from the encrusting action of lime on the paper machine and the ability to harden the paper by precipitation of silicate with aluminum sulfate. The pulp thus requires no washing in contrast with the use of about 40,000 gallons of water per ton of paper in the lime process.[103] The paper is of satisfactory quality, but the amounts of silicate required make the reagent cost greater than the cost of lime. Schwalbe [104] mentions the use of silicate solutions for the removal of straw, weeds, etc., from raw cotton fiber.

SOAP-SPARING ACTION OF SILICATE SOLUTIONS.

Precipitation of Calcium and Magnesium from Hard Water by Silicate. Decomposition of soap by reaction with calcium and magnesium compounds from hard water is costly for several reasons. Soap which takes part in the reaction is not available for washing. The insoluble soaps formed constitute dirt, which, on account of its adherent character, is exceptionally difficult to remove. Even though enough soap be used it is difficult to attain satisfactory cleansing and the color and feel of the fabric are inferior.

An ideal addition to soap would be one capable of reacting completely with hard waters without forming any insoluble soaps. Such a material is not known. Silicate solutions, like soaps, are able to precipitate quantitatively the calcium and magnesium from hard water. Richardson [105] investigated the problem of what occurs when both are present in the same solution, to find whether softening of the water would be at the expense of silicate or soap. He found that both the typical reactions, in which calcium chloride represents hard water and sodium oleate represents soap, take place.

1. $CaCl_2 + 2Na(C_{18}H_{33}O_2) = Ca(C_{18}H_{33}O_2)_2 + 2NaCl$
2. $CaCl_2 + Na_2O, 3SiO_2 = CaO, 3SiO_2 + 2NaCl$
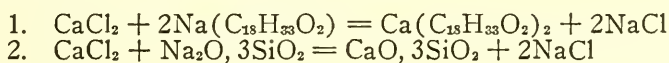
He found that the calcium silicate precipitate could react with calcium soap in reversible fashion, of which the following is typical:

3. $Ca(C_{18}H_{33}O_2)_2 + Na_2O,3SiO_2 \rightleftarrows CaO,3SiO_2 + 2Na(C_{18}H_{33}O_2)$.
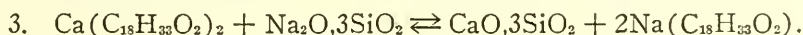
The equilibrium of such a system will determine the distribution of water-softening effect but with such complicated materials as soaps and silicates an exact interpretation seemed hopeless. The following general conclusions were reached:

[103] Dedrick, C. H., U. S. Pat. 1,682,834 (Sept. 4, 1928).
[104] Schwalbe, "Chemie der Cellulose," 1911, Berlin: Gebrüder Borntraeger.
[105] Richardson, A. S., *Chem. & Met. Eng.*, **25**, 594 (1922); *Ind. Eng. Chem.*. **15**, 241-243 (1923); *J. Soc. Chem. Ind.*, **42**, 364A.

"1—The distribution of the water-softening effect of a silicated soap between silicate and true soap will depend primarily upon the relative solubility of the precipitated soap and the precipitated silicate.

"2—The relative solubility of precipitated soap and precipitated silicate may vary with the nature of the soap, the composition of the silicate, the nature of the hardness of the water, and with the temperature.

"3—Other things being equal, increase in the proportion of true soap in the mixture favors water-softening at the expense of soap and increase in the proportion of sodium silicate favors water-softening at the expense of silicate.

"With reference to possible differences due to differences in the character of the true soap, preliminary experiments indicated no essential differences in the soap-sparing effect of sodium silicate when mixed with sodium oleate and when mixed with a selected commercial brand of 'pure' soap. The subject was not pursued further, and sodium oleate (from Eastman's 'practical' oleic acid) was used throughout the remaining experiments. Sodium oleate solutions have the very great practical advantage of not forming gels except at high concentrations."

The soap-sparing effect with various soaps indicated no essential difference.

"The effect of varying the composition of the sodium silicate was studied in some detail. Within practical limits the water-softening action of a given amount of sodium silicate of varying composition showed little change, except that increasing Na_2O content of the silicate resulted in a slight but distinct increase in its water-softening action toward temporary hardness. In all the experiments reported in detail in the present paper, the composition of the silicate used was Na_2O, $2.83SiO_2$.

"**Effect of Different Types of Hardness and of Temperature.** The effect of different types of hardness and the effect of temperature upon the efficiency of sodium silicate as a water softener in the presence of soap is very marked, as illustrated in the experiments of Tables [96 and 97]. In these experiments 50 cc. of the various hard waters mentioned in the tables were titrated at room temperature, 28°C. (± 1.5), and at the boiling point with a solution containing 1 gram of sodium oleate per 100 cc. In the room temperature experiments, the titration was carried out in a four ounce tall form bottle and at frequent intervals the bottle was shaken in an approximately uniform manner. In the experiments at the boiling point, the same amount (50 cc.) of the various hard waters was boiled in a 200 cc. round bottom flask at a slow and approximately uniform rate. In each case the amount of soap

necessary to produce a distinct foam and the amount necessary to fill the vessel with foam was determined. The same procedure was repeated after first adding to 50 cc. of each of the hard waters 1.5 cc. of a 5 per cent solution of sodium silicate (0.075 gram solid).

"The temporary hard water was a calcium bicarbonate solution originally containing 600 parts $CaCO_3$ per million, but at the time of its use the hardness had been reduced to approximately one-half this value by precipitation and sedimentation. The St. Bernard tap water, which is a deep well water, showed a hardness of 330 parts ($CaCO_3$) per million by the soap method. A complete analysis of the St. Bernard water was not made, but by analogy with similar water from the same neighborhood it may be assumed that the normality of the magnesium present was about one-half that of the calcium present.

TABLE 96. *Showing Grams of Sodium Oleate Necessary to Produce Foam from 50 cc. of Various Hard Waters, with and without 0.075 g. Sodium Silicate Added to the Water.*

Nature of Hard Water		0.0025M $CaCl_2$	0.0025M $MgCl_2$	Temporary Hardness	St. Bernard Tap Water
Without silicate	28°C.	0.10	0.11	0.15	0.17
With silicate	28°C.	0.10	0.01	0.15	0.12
Without silicate	100°C.	0.10	0.09	0.04	0.125
With silicate	100°C.	0.01	0.01	0.01	0.01

TABLE 97. *Showing Grams of Sodium Oleate Necessary to Fill Vessel with Foam from 50 cc. of Various Hard Waters, with and without 0.075 g. Sodium Silicate Added to the Water.*

Nature of Hard Water		0.0025M $CaCl_2$	0.0025M $MgCl_2$	Temporary Hardness	St. Bernard Tap Water
Without silicate	28°C.	0.145	0.22	0.20	0.30
With silicate	28°C.	0.15	0.13	0.20	0.19
Without silicate	100°C.	0.145	0.115	0.08	0.155
With silicate	100°C.	0.09	0.01	0.11	0.09

"Tables [96 and 97] indicate that sodium silicate is much more effective toward magnesium hardness than toward calcium hardness and also much more effective at 100°C. than at room temperature. Confirmation of these conclusions is obtained from the experiments shown in tables [98 and 99], in which the same hard waters were titrated in the same manner as described above, except that the silicate was not added separately, but was introduced by using a solution containing 1 gram sodium oleate with 0.5 gram sodium silicate per 100 cc.

"Table [100], which is for the most part self-explanatory, shows some of the typical results of our further study of the effect of temperature, and also the effect of the proportion of silicate used, upon the water-softening or soap-sparing action of sodium silicate. The experi-

TABLE 98. *Showing cc. of Soap Solution Necessary to Produce Foam from 50 cc. of Various Hard Waters, with and without Addition of Sodium Silicate to the Soap Solution.*

Nature of Hard Water		0.0025M $CaCl_2$	0.0025M $MgCl_2$	Temporary Hardness	St. Bernard Tap Water
Without silicate	28°C.	10	11	15	17
With silicate	28°C.	10	9	14	13
Without silicate	100°C.	10	9	..	12.5
With silicate	100°C.	7	3	..	4

TABLE 99. *Showing cc. Soap Solution Necessary to Fill Vessel with Foam from 50 cc. of Various Hard Waters, with and without Addition of Sodium Silicate to the Soap Solution.*

Nature of Hard Water		0.0025M $CaCl_2$	0.0025M $MgCl_2$	Temporary Hardness	St. Bernard Tap Water
Without silicate	28°C.	14.5	22	20	30
With silicate	28°C.	15	20	19	21
Without silicate	100°C.	14.5	11.5	..	15.5
With silicate	100°C.	10	5.5	..	6.5

ments at 25°, 50°, and 75°C. were carried out according to the room-temperature procedure already described, except that a water bath was used for temperature control.

TABLE 100. *Showing cc. of Solution Containing 1 Gram Sodium Oleate per 100 cc. Together with Varying Amounts of Sodium Silicate, Necessary to Produce Foam from 50 cc. St. Bernard Tap Water at Various Temperatures.*

Grams silicate per 100 cc. soap solution	0.0	0.1	0.2	0.3	0.4	0.5	1.0	2.0	4.0
Temperature									
25°C.	17	17	17	16	16	13	11	10	10
50°C.	17	16	14	13	13	13	..	..	..
75°C.	15	14	13	13	13	13	..	..	..
100°C.	12.5	6	5	4	4	4	2	1	0.5

"The results shown in Table [100] not only show an increase in the water-softening by silicate as the proportion of silicate to soap increases, but also show that a certain minimum of silicate must be present with soap in order to effect any water-softening at all by silicate. At ordinary temperature this minimum is considerable, even for a hard water high in magnesium. At 100°C., however, any practical quantity of sodium silicate was found to have a distinct soap-sparing effect. In fact, careful analysis of the table will show that in some cases the apparent weight of soap conserved per gram of silicate used was several times the theoretical value calculated from reactions (1) and (2). We are at a loss to explain so great a discrepancy, although it is partially explained by the fact that soap wastage is greater than indicated by reac-

tion (1), much sodium soap being dragged down by the insoluble soaps.

"Since much of the water supply of this country is quite hard and since a considerable proportion of the household laundry work, if not the greater part of it, is done at 100°C., it is highly probable that the water-softening action of sodium silicate has been a large factor in the success of silicated soaps. The above experiments, however, emphasize the impossibility of prescribing an ideal amount of silicate for use in such soaps, because each kind of hard water and each washing temperature present a separate problem."

Vincent found that a mixture of 20 per cent soap and 80 per cent silicate was practically twice as effective as pure soap for softening water containing iron and that the advantage of adding the silicate separately before the soap was very small. Sodium silicate is much better than sodium carbonate for this purpose on account of the silicate's ability to form a negative sol. The iron is dispersed rather than precipitated.

EFFECTS ON FABRICS.

Control of Alkalinity. Perhaps the most important effect of colloidal silica in detergent processes is its ability to modify the action of sodium oxide and to resist changes in hydroxyl ion concentration. It has already been shown that sodium is adsorbed on silica in solution,[106, 107] and we shall have further occasion to deal with this property in considering gels. *Solutions of soluble silicates do not behave like solutions containing the same concentrations of sodium as hydroxide.* The more silicious grades actually reduce the alkalinity of soap-sodium carbonate mixtures used in ordinary laundry practice. In these respects the silica is analogous to fatty acids in soap. The concept of the multi-charged colloidal micelle explains the high conductivity in dilute solution and fits the facts of experience with detergent processes using either silicates or soaps. Adsorbed sodium is much less active than free caustic alkali.

Glass bottles cleaned with hot dilute sodium hydroxide or carbonate solutions soon become dull and unattractive. Silicate solutions after thorough rinsing leave the glass lustrous.

Ordinary tin plate is quickly discolored on contact of a few days with cold sodium hydroxide solutions. Exposure to a solution of Na_2O, $3.3SiO_2$ containing the same percentage of Na_2O leaves the tin bright.

[106] Bogue, R. H., *J. Am. Chem. Soc.*, **32**, 2575-2582 (1920).
[107] Stericker, Wm., *Chem. & Met. Eng.*, **25**, 61 (1921).

Accidental exposure of the sensitive tissues of the mouth to a 40 per cent solution of $Na_2O, 3.3SiO_2$ is a trifling annoyance. A like amount of Na_2O as hydroxide would cause a painful injury.

Strength of Fabric. In detergent use the modifying action of silica is shown by its effect on the strength of cotton fiber. A careful and extended study of Zänker and Schnabel showed that cotton washed in boiling solutions of soap and sodium carbonate with and without silicate would show the contrast between silicated and silicate-free detergent solutions. They used four materials:

1. Neutral boiled soap, 60 per cent cottonseed, 40 per cent palm kernel oil.
2. The same made with 20 per cent 1.38 specific gravity, $Na_2O, 3.3SiO_2$ and 5 per cent NaOH solution, presumably enough to produce $Na_2O, 2SiO_2$.
3. Washing powder, 30 per cent fatty acid, containing soap and Na_2CO_3 only.
4. The same, plus 20 per cent 1.38 specific gravity, $Na_2O, 3.3SiO_2$ and 5 per cent caustic soda lye.

The solutions contained 5 grams each of soap and soap powder per liter of water. It is to be noted that the conditions of this study, in which a relatively large amount of Na_2O was present, some of it added as hydroxide, were particularly severe. They also differed from ordinary washing in the absence of mechanical action on the fiber. The samples were boiled for an hour at each operation, though without mechanical agitation. The strength was determined by breaking individual fibers. The fiber was rinsed well after each washing, dried and allowed to come to equilibrium with the air before testing. Fifty measurements at least were averaged for each point (Fig. 155 and Table 101).
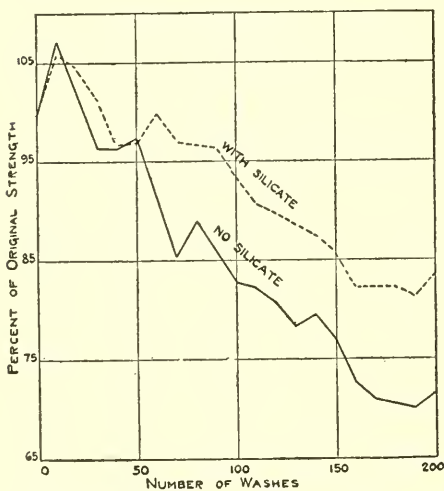
FIG. 155.—Effect of Silicate on the Strength of Cotton Fiber.

The strength increased slightly for the first ten washes, probably due to shrinkage or a slight mercerizing action. The increase was less in the silicated detergent and the final loss of strength after many washes was smaller. This can only mean that the silica has a modifying effect on the alkali in washing. The assumption of Zänker and Schnabel [108] that the weakening of the fiber is a measure of detergency and that these experiments show soap to be a more active washing agent is not warranted in view of the complex nature of the washing process.

[108] Zänker and Schnabel, *Seifenfabrikant,* 37, 249-253, 279-282 (1917).

Kind [109] recognized how difficult it is to perform washing experiments with only one variable and obtain consistent results. He used Na_2O, $3SiO_2$ and found an increase of strength in cotton fiber after 30

TABLE 101. *Effect on the Strength of Cotton Fiber of Silicates in Detergents.*

	Strength, Per Cent	
Number of Washings	Without Silicate	With Silicate
0	100.00	100.00
10	107.02	105.84
20	102.13	104.62
30	96.29	101.58
40	96.28	96.69
50	97.30	96.87
60	91.52	99.89
70	85.32	97.17
80	88.72	96.65
90	86.09	96.48
100	82.74	93.36
110	82.30	90.66
120	81.03	89.91
130	78.28	88.82
140	79.39	87.50
150	77.06	85.83
160	72.58	82.22
170	70.89	82.20
180	68.24	82.24
190	70.14	81.36
200	71.56	83.38

washes but a loss on linen after the same treatment about twice as great as that caused by an olive oil soap. Heermann [110] also found small losses with 50 washes when detergents containing silicate were used, less than 5 per cent on cotton and 14 per cent on linen, which compares favorably with pure soap.

Effect of Ash. Kind's high ash figures compared with Zänker and Schnabel are probably due to inadequate rinsing, and this condition may also have something to do with the loss in strength of linen fiber.[111-113]

Some statements indicating an injurious effect of the silica deposit upon fibers require examination because they have been widely quoted. It has been said that the deposited silica takes up water, expands, and disrupts the fiber. No experimental evidence is offered in support of

[109] Kind, W., "Die Wirkung der Waschmittel auf Baumwolle und Leinen," Ziemsen, Wittenberg and Halle, **1902**; *Chem. Ztg.*, **47**, 457-460, 484-485 (1923).
[110] Heermann, P., *Z. angew. Chem.*, **36**, 101-103, 106-111 (1923); *Mitt. Material-prüfungsamt*, **39**, 65-72 (1921); *C. A.*, **17**, 885; cf., *C. A.*, **15**, 2993.
[111] Heermann, P., and H. Somner, *Textilberichte*, **3**, 238 (1922).
[112] Farrel and Goldsmith, *J. Soc. Ryers Colourists*, 195 (1910).
[113] Leimdörfer, J., *Seifensieder Ztg.*, 1271 (1908); **48**, 519-520, 539-541 (1921); *C. A.*, **15**, 3406.

TABLE 102. *Effect of Detergents on Strength and Ash of Cotton and Linen Fiber.*

(Kind)

Original Breaking Strengths { Cotton Fiber = 524 gm. / Linen Fiber = 1078 gm.

C = Condenser Water, T = Tap Water.

25 gm. of fiber treated in 600 cc. water each time. Contents of bath given as percentages of this liquor (600 cc.).

Bath	Kind	Per Cent of Original Strength After Being Washed						Ash Content in Per Cent after 30 Washings			
		10 Times		20 Times		30 Times		Cotton		Linen	
		Cotton	Linen	Cotton	Linen	Cotton	Linen	Total	SiO_2	Total	SiO_2
Water	C	102	97	99	95	101	94	0.30	…	0.30	…
	T	114	108	100	101	101	91	0.34	…	0.44	…
2% soap	C	112	94	95	84	94	84	1.40	…	0.52	…
	T	102	95	106	93	90	88	1.54	…	0.72	…
2% soda ash	C	115	87	107	92	112	74	4.14	…	2.51	…
	T	106	89	113	89	103	84	6.26	…	2.56	…
2% Na_2O, $3.3SiO_2$, 38° Baumé	C	125	98	123	70	125	74	9.70	8.78	10.52	9.78
	T	122	97	124	99	112	74	14.16	11.84	9.60	8.22
1.5% silicate / 0.5% caustic soda	C	135	100	116	87	128	83	5.82	3.28	6.92	4.22
	T	122	92	117	86	110	73	5.66	3.22	5.84	3.60
1% soap / 1% soda ash	C	115	70	103	54	96	36	1.92	…	3.56	…
	T	102	54	104	43	101	29	6.12	…	7.80	…
1.5% soap / 0.5% caustic soda	C	105	91	102	78	98	73	0.78	…	0.78	…
	T	92	92	103	69	97	70	1.12	…	1.10	…
1% soap, ¾% soda / ¼% silicate	C	105	87	111	59	100	51	1.32	0.54	2.26	0.78
	T	103	78	104	56	100	44	4.40	1.82	6.74	2.32
1% soap, ⅝% soda	C	124	83	117	60	119	50	1.92	0.78	3.76	1.24
⅛% caustic, ¼% silicate	T	89	91	103	49	99	36	3.63	1.60	6.36	2.18
2% washing powder and silicate	T	116	58	115	54	112	44	10.46	3.84	12.00	4.38
Same, no silicate	T	96	76	107	52	98	40	3.38	…	5.98	…
Same, plus silicate and bleach	T	102	91	108	79	102	49	5.48	2.96	6.40	3.72

TABLE 103. *Effect on the Ash of Cotton Fiber of Silicates in Detergents.*
(Kind)

		Per Cent Ash
Original ash content of the fiber		0.45
Detergent without silicate after 10–100 washes		0.45–0.60
Detergent with silicate, number of washes....	10	0.95
	20	1.82
	30	2.35
	40	3.16
	50	4.12
	60	5.14
	70	5.45
	80	5.75
	90	6.57
	100	6.92

this.[114]   Silica is always deposited in a hydrous condition from silicate solutions under conditions appropriate to washing.   The hydrous silica contracts on drying, and like other silica gels does not increase in volume when put into water.   Further, examination of the fibers under a microscope does not reveal that those containing high ash are broken after many washings with ironing between, and there is no evidence that the deposit depreciates the strength of the fiber, and only when the deposit is large is there any noticeable tendency toward a harsh feel or added stiffness.[115]   Linen, silk, and wool are somewhat more affected by silicate solutions than by neutral soaps, but this must be regarded as a result of the somewhat greater alkalinity of the silicates used.   In short, the rather persistent idea that silica in wash liquors is harmful appears to be the inheritance of an older literature rather than the result of systematic study in the light of present knowledge, not only of chemical theory, but of the behavior of soluble silicates.[116-126]   The tradition has come

[114] Keilmeyer, "Farberlehrling," p. 73, from Schwalbe, "Die Chemie der Cellulose," Berlin: Borntraeger, 1911.
[115] Zänker and Schnabel, *loc. cit.*
[116] Vohl, *Berliner Musterzeitung* (1872).
[117] Calvert, *J. Chem. Soc.*, 18, 70-77 (1865).
[118] Schelhass, *Bayerisches Gewerbeblatt*, 203 (1872).
[119] Euler, F., *Leipziger Färber Ztg.*, 59, 81-82; *C. A.*, 4, 1240 (1910).
[120] Leimdörfer, J., *Seifensieder Ztg.*, 48, 519-520, 539-541 (1921); *C. A.*, 15, 3406.
[121] Grün, A., and Jungmann, *Seifenfabr.*, 37, 507-510, 529-531, 553-555, 579-581, 603-606 (1917); *J. Soc. Chem. Ind.*, 37, 411A; *C. A.*, 12, 2693.
[122] Romagnoli, A., *Seifensieder Ztg.*, 33, 67 (1906); *Chem. Zentr.*, 77, 1, 714 (1906.)
[123] Kühl, H., *Chem. Ztg.*, 43, 354-355 (1919); *J. Soc. Chem. Ind.*, 38, 589A; *C. A.*, 13, 3018.
[124] Chevreul, "Recherches chimique sur les crops gras d'origin animals" (Paris, 1815-1823, reprinted 1889).
[125] Berzelius, *Muspratts Handbuch der tech. Chemie*, 6, 3rd ed., 1067 (1874-80).
[126] Davidsohn, J., and G. Weber, *Seifensieder Ztg.*, 35, 775, 798-800; *Chem. Zentr.*, 79, II, 836 (1908); *C. A.*, 3, 1224.

down into some rather recent writings, but there are now reports available from which a clearer appraisal of the facts may be gleaned.[127-129] It is sufficiently evident that undesirable results can be had by using the wrong silicate or the wrong concentration, and some of the conflict
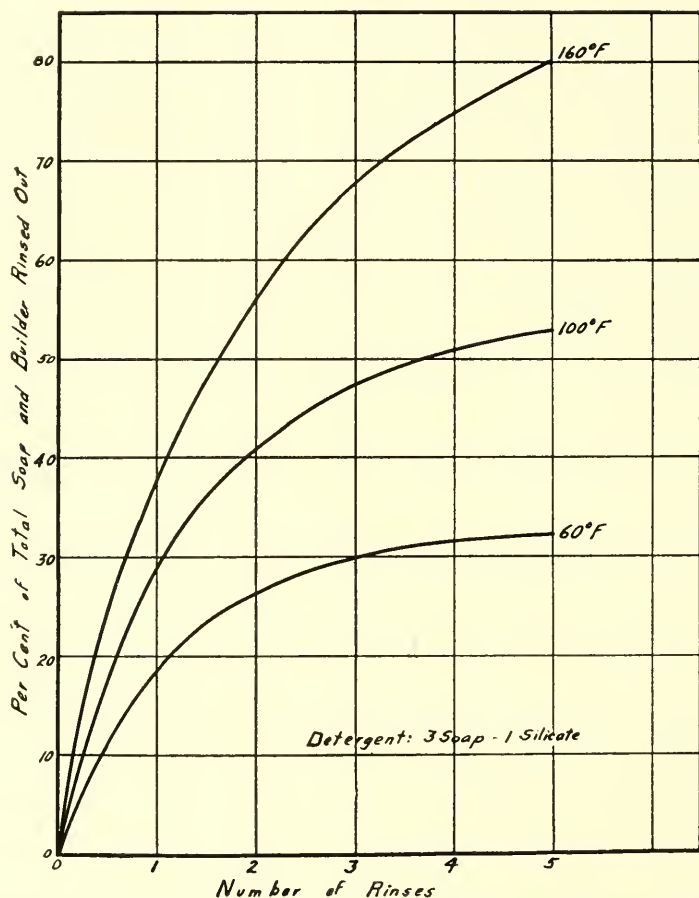
Fig. 156.—The Effect of Temperature on Rinsing Efficiency.

of statement is doubtless due to the use of different or unsuitable silicates or conditions, often to both.[130-135]

Rinsing. It has been suggested that silicate detergents might not

[127] Löffl, K., *Kunststoffe,* **6,** 239-40 (1916) ; *C. A.,* **11,** 1327.
[128] Schwalbe, "Die Chemie der Cellulose," Berlin : Gebrüder Borntraeger, **1911.**
[129] *Rev. chim. ind.,* 266 (1924) ; *Text. Inst.,* **16,** A 203 (1925).
[130] Zänker and Schnabel, *loc. cit.*
[131] Kind, W., "Die Wirkung der Waschmittel auf Baumwolle und Leinen," Ziemsen, Wittenberg and Halle, **1902.**
[132] Vail, J. G., *Chem. Age,* **30,** 19-20 (1922) ; *C. A.,* **16,** 993.
[133] Jackson, H., "Cantor Lectures on Detergents and Bleaching," London : Trounce, **1907.**
[134] Vail, James G., *Chem. & Met. Eng.,* **31,** No. 5, 183-184 (1924).
[135] Stericker, Wm., *loc. cit.*

be readily removed in the rinsing process. The slow building up of ash in the fiber is a partial answer. Direct comparison of the removal of alkaline salts used with soap under conditions encountered in laundry practice shows that a certain silicate-carbonate mixture was not as completely removed by a given amount of rinsing at 60°F. as carbonate alone but at 160°F. the silicate mixture was slightly better than
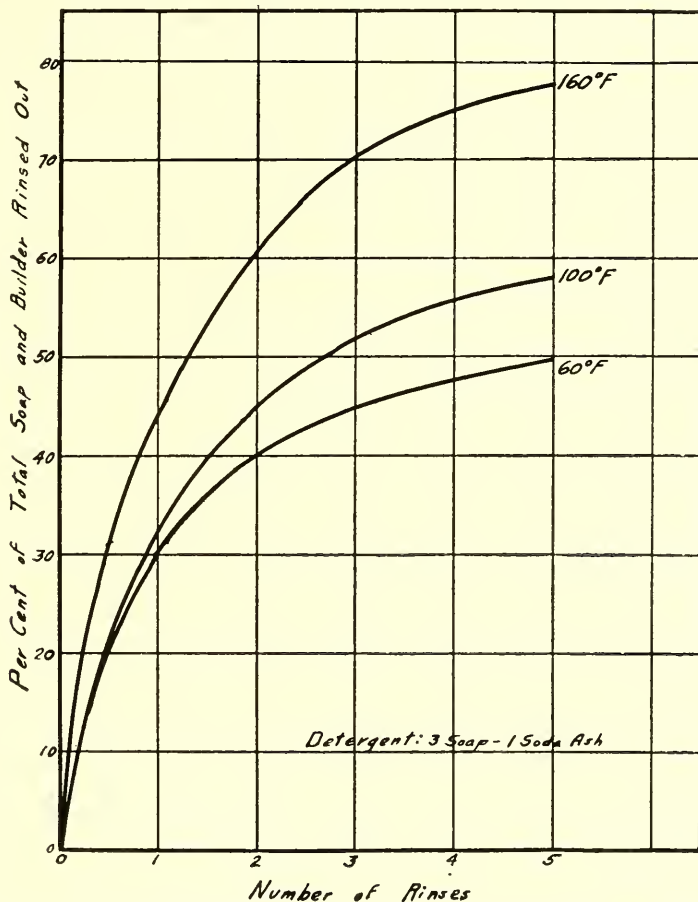
FIG. 157.—The Effect of Temperature on Rinsing Efficiency.

the carbonate as shown in Figures 156 and 157. Rinsing properties should not therefore be a bar to the use of silicate detergents.[136]

Action on Various Fabrics. Stericker [137] tested various fabrics by soaking in 5 per cent solutions of a series of silicates from Na_2O, $3.9SiO_2$ to Na_2O, $1.6SiO_2$ at 20° and 80°C. and compared the effects of sodium carbonate and sodium hydroxide. The samples were rinsed in distilled water and examined microscopically. $Na_2O,2SiO_2$ and the more

[136] Procter and Gamble Research Staff, *Laundry Age*, 182 (April 1, 1927).
[137] Philadelphia Quartz Company, unpublished report of.

alkaline silicates increased the luster of cotton, but the fibers did not swell, as in a sodium hydroxide solution.[138, 139]

Twenty strips of cotton sheeting, 1 inch wide, were soaked in the solutions indicated for 3 hours.[140] The solutions were maintained at 63°C. during the entire time. The tensile strength of the strips was then determined on a motor-driven Scott tester. The strips were tested while wet in order to eliminate errors due to differences in humidity. Each run was duplicated so that the figures given below represent the average of forty tensile strength determinations.

Material	Concentration		
	0.05%	0.5%	5.0%
Water	37.5		
$Na_2O, 3.34SiO_2$	...	37.6	37.7
Soda ash	37.5	37.3	37.0
Caustic soda	39.2	38.0	31.7

It will be noted there is practically no change in strength with Na_2O, $3.34SiO_2$ or soda ash. In concentrations below 0.5 per cent, caustic soda increased the strength but at 5.0 per cent caused a decided decrease.

"The following tests were run on samples of all silk crêpe de chine. Five per cent solutions of $Na_2O, 2.47SiO_2$, $Na_2O, 3.34SiO_2$, and Na_2O, $3.96SiO_2$, and of soda ash had no appreciable effect on this silk either at room temperature for 23 hours or at 63°C. (176°F.) for 3 hours. Since $Na_2O, 2.47SiO_2$ is the most likely of these three silicates to cause damage, a sample of silk was soaked in it for a week at room temperature. Even at the end of that time there was no evidence of damage. Nineteen hours at room temperature in 5 per cent solutions of Na_2O, $1.62SiO_2$ and $Na_2O, 2.03SiO_2$ did not injure samples of silk, but 3 hours at 63°C. was sufficient to damage them. With $Na_2O, 1.62SiO_2$, the woof threads were thinned to about half their normal size. With Na_2O, $1.23SiO_2$ there was evidence of tendering, but not nearly to such a great degree. Caustic soda at room temperature destroyed a portion of the silk and greatly tendered the remainder. At 63°C. it dissolved the silk entirely.

"With samples of flannel, only part of which was wool, the most delicate indication of injurious action was the appearance of a yellow color in the solution used to soak the samples. At room temperature after 19 hours there was only a barely perceptible yellowish tinge with $Na_2O, 3.34SiO_2$ and $Na_2O, 3.96SiO_2$. The solution of soda ash

[138] *Rev. chim ind.*, 266 (1924) ; *Text. Inst.*, **16**, A, 203 (1925).
[139] *J. Home Economics*, **17**, No. 12, 728 (1925).
[140] Danley, Mary, personal communication.

and the other brands of silicate were distinctly yellow while the caustic soda solution was very yellow. Under these conditions the caustic had dissolved all the wool. $Na_2O, 1.62SiO_2$, $Na_2O, 2.03SiO_2$, and $Na_2O, 2.47SiO_2$, and soda ash all seemed to dissolve some wool. The amount dissolved decreased in the order named. The flannel remained soft in all cases.

"At 63°C. the action of these materials was intensified. At the end of 3 hours not only caustic soda but $Na_2O, 1.62SiO_2$ as well had dissolved all the wool. $Na_2O, 2.03SiO_2$ had left spots of wool and $Na_2O, 2.47SiO_2$ about half of the original amount. Soda ash had dissolved enough to be perceptible but $Na_2O, 3.34SiO_2$ and $Na_2O, 3.96SiO_2$ had not. Wherever there was any wool left, it had become yellow and was matted. When wet, it was slippery and slimy. When dry, it was stiff and hard. It will be recognized that these tests are very drastic and simply show tendencies, as the use of alkalies at this concentration and temperature is unheard of."

Linen is similar to cotton in that it is essentially cellulose. Since there was no damage to cotton and since cellulose is not injured by dilute solutions of alkaline salts, it is believed that the various grades of silicate of soda will have no effect on it. It seems at least safe to say that $Na_2O, 3.34SiO_2$ and $Na_2O, 3.96SiO_2$ will not injure it in any way. The same reasoning applies to viscose, Chardonnet, and cupra-ammonium rayons since all of these are essentially cellulose. No predictions are offered concerning cellulose acetate rayon.

These tests do not represent working conditions since the concentration of any of these materials in the wash-wheel should not exceed 0.5 per cent (one-tenth the amount used here). They intensify any possible injurious action so it can be discovered in a few days or hours in place of the many weeks required in actual laundry practice. Any recommendations based on these experiments therefore will err on the side of over-caution.

Effect on Color. The silicate solutions have been shown to exercise a protective effect on cotton in the wash, as compared with soap and sodium carbonate mixtures. Colors are also more permanent when silicate is used in the wash. Every soap maker knows that the more silicious types will reduce the free alkalinity of soap [141] but even these exercise a more active effect upon the skin than a neutral soap.[142] Strong silicate solutions should not be recommended for the bath or for washing the most delicate silks and woolens. More data are needed, though

[141] Zänker and Schnabel, *loc. cit.*
[142] Edeler, A., *Ind. Eng. Chem.*, **17**, 196-197 (1925),

some very successful washing of flannels has been done with washing powders containing silicate, and there is evidence that with control of ratio and concentration it may have a place both in scouring raw wool and in degumming silks.[143-147]

It should be pointed out, however, that the concentration of ratio 1 : 4 of 0.25 per cent found by Fall to give maximum deflocculation had a pH of only 9.4 in distilled water, was scarcely perceptible to the taste and did not cause a slimy feeling when rubbed on the hands. Its alkalinity is very mild.

In addition to its restraining action on alkali and its effect on the ash of textile fibers, colloidal silica in the wash resists the tendency of cotton goods repeatedly washed in sodium carbonate to turn gray. It has been assumed that the whitening action of silicate detergents was the result of the deposition of silica, which builds up in the fibers. If this were so we should expect colored goods to assume a dull or milky cast, but actually they are brighter than when no silicate is present.

This may be partly due to the much lower solubility of dyestuffs in silicate or silicate soap mixtures than in solutions of pure soap.[148]

McDowell[149] believes that the better color of dyed goods which have been treated with silicate solutions is due to the deposition of a protective film. He found indanthrene and other vat colors after kier treatment in the presence of silicate became insensitive to chlorine bleach to such an extent that goods with designs in color could be bleached by the methods ordinarily used for "gray" goods without the need of any after treatment to restore an altered color.

Carter[150] found that the improvement in color of white goods did not run parallel to the increment of ash, and also that the ash could be almost completely removed without sacrifice of the better color in comparison with goods having identical treatment except for the silicate.[151-152] The explanation of this effect on color remains to be found, but something may be learned by analogy in considering the soluble silicates in bleaching processes.

Peroxide Bleaching. Peroxide bleaching is best done in a mildly

[143] Thies, F., *Z. angew. Chem.*, **36**, 312-314 (1923) ; *C. A.*, **17**, 3424.
[144] Milson, J. R., U. S. Pat. 1,430,099 (1922).
[145] *Am. Chemist*, **2**, 357 (1872).
[146] Van Baerle and Company, *J. Soc. Arts*, **20**, 840 (1872).
[147] Grothe, H., *Musterzeitung*, **24**, 340 ; *Chem. Zentr.*, **46**, Ser. 3, **6**, 830 (1875).
[148] Vincent, G. P., *J. Phys. Chem.*, **31**, 1305 (1927).
[149] McDowell, J. D., U. S. Pat. 1,558,104 (Oct. 20, 1925).
[150] Carter, J. D., *Ind. Eng. Chem.*, **18**, No. 3, 248 *et seq.* (1926).
[151] Zänker and Schnabel, *loc. cit.*
[152] Grothe, H., *Musterzeitung*, **24**, 378 (1876) ; *J. Chem. Soc.*, **31**, 757 (1877) ; *Chem. Zentr.*, **7**, 92-93 (1876).

alkaline bath from which oxygen is liberated in such a way as to give maximum bleaching effect. When colloidal silica is present, the bath, though still effective for bleaching, is stabilized and does not decompose or lose oxygen on standing at the rate which obtains when alkaline compounds other than silicate are used. Silicates also act as preservatives and stabilizers for solid bleaching compounds which decompose in water to yield hydrogen peroxide.[153-161] Such are perborates, percarbonates, persulfates, and peroxides of the alkali metals.

Weber [162] compared the losses of oxygen from a one-volume bath of hydrogen peroxide at 37°C. without the addition of alkali and with varying quantities of ammonia and silicate, probably about Na_2O, $2SiO_2$. When no ammonia or silicate was added there was no loss of hydrogen peroxide. With addition of 0.5 cc. of 0.897 specific gravity ammonia to 500 cc. of 1 volume hydrogen peroxide, the loss in 3 hours was 20 per cent of the hydrogen peroxide present, and ten times this amount gave a loss of 69.7 in the same time. Under like conditions with silicate the maximum loss of hydrogen peroxide in the baths was less than 1 per cent, i.e., probably not greater than the experimental error.

Peroxide baths neutralized with silicates are suitable for bleaching wool, silk, cotton, and rayon, or fabrics in which these fibers are mixed. When a close adjustment of alkalinity is necessary, baths should be made up a day before using because the silicate solutions are more alkaline when first made up than they are after coming to equilibrium.

The experiments shown in Figure 158 were made in the absence of fiber, but trials with 135 to 180 kilos (300 to 400 pounds) of wool showed that one third the cost of hydrogen peroxide can be saved by neutralizing with silicate of soda.[163]

"If too much silicate is used, it will give a yarn rather harsh to the touch; for example, 2.265 kilograms of silicate to 90.86 liters hydro-

[153] Schaidhauf, Alois, U. S. Pat. 1,225,872 (May 15, 1917).

[154] Wade, Harold, Ger. Pat. 152,366 (Oct. 21, 1920)

[155] Kind, W., *Seifensieder Ztg.*, **42**, 598-599 (1915); *C. A., 9*, 2971; *Textilberichte*, **2**, 325-326 (1921); *C. A.*, **16**, 2416.

[156] Palmetto, *Textile World J.*, **52**, No. 17, 29 (1917); *C. A.*, **11**, 1550.

[157] Deutsche Gold und Silber Scheideanstalt, Ger. Pat. 357,956 (March 13, 1919); *Chem. & Met. Eng.*, **28**, 33 (1923); Aus. Pat. 98,668 (May 29, 1922); Brit. Pat. 196,839 (June 6, 1922); *C. A.*, **17**, 3760.

[158] Moore, K. R., *Am. Dyestuff Reptr.*, **7**, No. 19, 11, 16-17 (1920); *C. A.*, **15**, 1221.

[159] Surpass Chem. Co., Brit. Pat. 158,531 (1920).

[160] *C. A.*, **15**, 2000.

[161] Roessler, Ger. Pat. 357,956.

[162] Weber, G., *J. Soc. Dyers Colourists*, **39**, 209-214 (1923).

[163] Weber, *loc. cit.*

gen peroxide (5 pounds of silicate to 20 gallons hydrogen peroxide), 12 volumes, will give a harsh yarn. But it is possible to use silicate of soda and obtain a bleached wool beautifully soft and full, unimpaired in every way, and for this only 0.453 kilogram silicate of soda (1 pound) should be used for 90.86 liters of 12 volume hydrogen peroxide. The white obtained also is better than that given with a bath neutralized with ammonia. In addition, it has a protective influence, and any iron which may accidentally be present in the goods or any copper in the form of stains, will not damage the fiber in the presence of silicate of soda. The bath will last with continuous replenishing for one week to a month, depending on the quality of the yarn used.
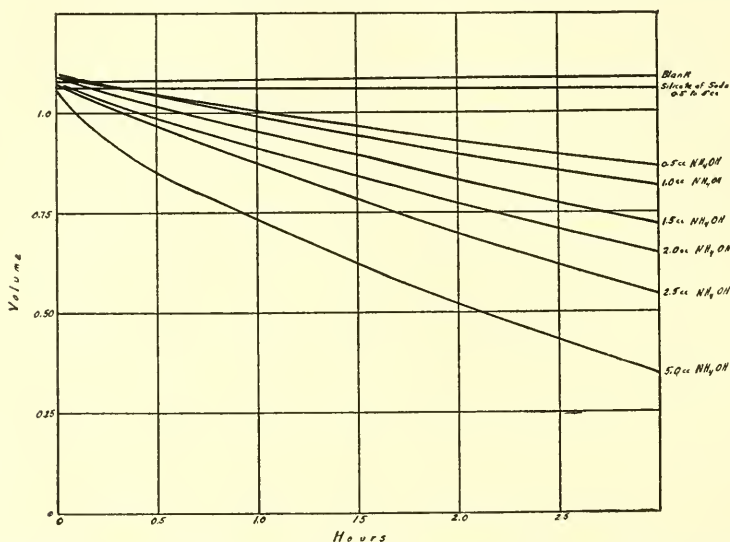
FIG. 158.—Deterioration of Peroxide Baths Neutralized with Ammonia and Silicate of Soda.

Piece goods are bleached in jiggers; a six volume bath gives the best results, and here again silicate of soda should be used for neutralizing. Hydrogen peroxide gives equally good results with botany or crossbreds, either with yarn or finished goods.

"In order to obtain uniform results, it is important to standardize the methods of working for the particular quality of the goods under treatment, using the weight of goods as a basis.[164] The same concentration of liquor, the same quantity of sodium silicate, and the same temperature should be used for each lot."

The action of hydrogen peroxide is catalytically stimulated by ferric oxide, often to the extent of causing holes in silk or wool fabrics on which particles of rust have lodged. Other substances have a similar

[164] Smolens, H. G., *Oil, Paint, Drug Rep.,* **109**, No. 13, 60 (1926).

effect and dirty goods always lose more strength than clean in hydrogen peroxide bleaching.[165]

A commercial formula for cotton bleaching with sodium peroxide is as follows:

To 100 gallons of cold water, add:

  4¾ lbs. 66° sulfuric acid. Heat to 100° F. and sprinkle slowly into the bath;
  4 lbs. sodium peroxide powder. Heat to 190° F. and add
  5 lbs. silicate of soda solution (NaO_2, 10.5%; SiO_2, 26.7%; Baumé 42°) which has been previously diluted in two gallons of warm water.

The protective action of silicates is probably due primarily to their ability to keep ferric hydroxide deflocculated [166] and thus unable to exert a local action, but inasmuch as the same action of silicates may be observed in cotton boiling with sodium hydroxide, in washing with soap, and in bleaching, it seems likely that the negatively charged silica tends to surround positively charged particles of ferric compounds with a film which prevents their adherence to fibers bearing a negative charge. If the film should form, it would mechanically prevent flocculation and appearance of the iron in spots. The protective action is not sufficient to prevent damage if actual rust specks are dropped on the fabric during bleaching. Silicates of very low iron content are demanded for this use, but it is doubtful if the iron ordinarily present in commercial silicates would do other harm than to increase the rate of liberation of oxygen. This is, however, important in some factories where the routine is on a strict time schedule.

Silk may be bleached in a bath containing peroxide, silicate, and soap for 8–12 hours at 50°C.[167, 168]

Peroxide baths can be used to bleach whites in striped goods where the color may be fast to peroxide and sensitive to chlorine bleach. They are also of use for stripping colors which are sensitive to peroxide.[169-171]

Smolens [172] has found that wool and silk as well as their mixtures with cotton may be advantageously bleached in baths containing more peroxide and much more silicate than formerly thought permissible,

[165] Heermann, P., *Z. angew. Chem.*, **36**, 107 (1923); *Z. deut. Öl- Fett-Ind.*, **41**, No. 22, 338-341 (1921).
[166] Grün and Jungmann, *Seifenfabrikant*, **37**, 507-510, 529-531, 553-555, 579-581, 603-606 (1917); *C. A.*, **12**, 2693.
[167] Emmons, *Am. Dyestuff Rep.*, 382-384 (1923).
[168] Ley, "Seidenfärberei," Berlin: Julius Springer, 1921, p. 53.
[169] Humphries, R., *Textile Recorder*, **28**, 11-13 (1925).
[170] Reichert, J. J., Brit. Pat. 176,747 (June 13, 1921); *C. A.*, **16**, 2418.
[171] Kind, W., *Seifensieder Ztg.*, **49**, 761-762, 773-774, 785-786, 798 (1922); *C. A.*, **17**, 892.
[172] Smolens, H. G., personal communication.

thus securing good color in a short time without as much injury to the fiber as might have come from a weaker bath in a longer time.

Peroxide solutions which have been stabilized with phosphoric acid
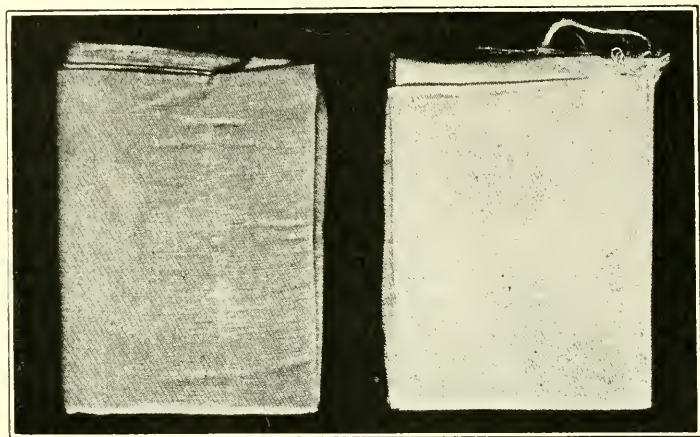
FIG. 159.—Effect on Cheesecloth of Sodium Hypochlorite Treatment with and without Silicate.

and neutralized with silicate solutions have the advantage of containing a buffer salt in addition to the silicate. This simplifies the control of baths which are continuously replenished by the addition of re-
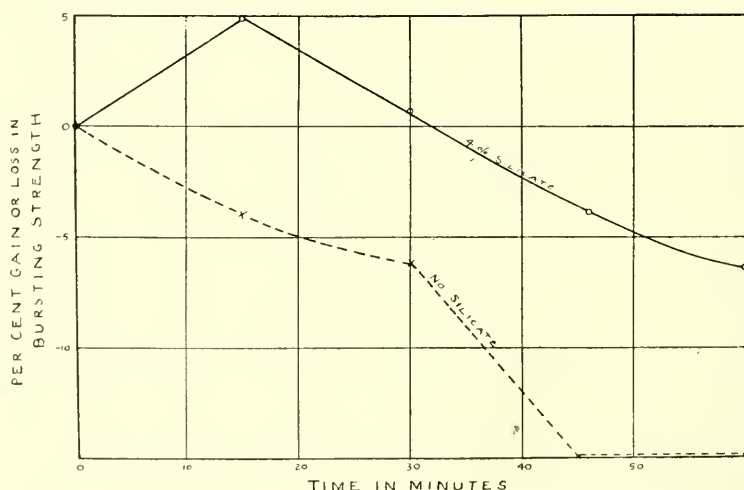
FIG. 160.—Effect on Cheesecloth of Sodium Hypochlorite Treatment with and without Silicate.

agents and increases the life of those which are used to exhaustion. Electrolytes have an unfavorable effect on the color obtainable and as the disodium phosphate formed is a poor electrolyte the phosphoric acid-sodium silicate bath is one of the most efficient.[173]

Hypochlorite Bleaching. Sodium hypochlorite, unlike hydrogen

[173] Smolens, H. G., *Oil, Paint, Drug Rep.* (March 22, 1926).

peroxide, is stabilized by silicate solutions only in the presence of bleachable material, but Carter [174] found that the weakening action of hypochlorite bleach was decreased by putting silicate solutions into the bleaching bath when the chlorine value is high enough to cause rapid attack on cotton goods. The effect on color is marked. When

Fig. 161.—Effect of Silicate with Sodium Hypochlorite Bleach on Sheets of Sulfite Pulp.

silicate is present a given amount of hypochlorite yields a much whiter colored cotton independent of the increment of ash.[175]

Wood pulps made by the sulfite process Carter found to give better colors when silicates were added to calcium hypochlorite baths. The results thus secured were better than could be had with any concentration of calcium hypochlorite alone.

TABLE 104. *Silicates Used in the Following Tests.*

No.	Per Cent Na$_2$O	Per Cent SiO$_2$	Mol. Ratio	°Bé.
1	10.5	26.7	1 : 2.60	42
2	19.4	30.6	1 : 1.62	58.8
3	8.9	29.0	1 : 3.33	41
4	13.7	32.9	1 : 2.56	52

TABLE 105. *Chlorine Values of Hypochlorite Solutions with and without Silicate.*

Chlorine Value, Grams in 25 cc.

Silicate No. 1 Grams	Original	After Warming to 49°C. for 1 Hour	Loss of Chlorine Gram	Per Cent
0	0.04342	0.04342	None	None
0.25	0.04342	0.04342	None	None
0.5	0.04342	0.04342	None	None
1	0.04342	0.04342	None	None
3	0.04342	0.04342	None	None
5	0.04342	0.04342	None	None

[174] *Ind. Eng. Chem.*, **18**, 248 (1926).
[175] Mandelbaum, R., Ger. Pat. 330,192 (1920) ; *C. A.*, **17**, 858.

TABLE 105. *Changes in Chlorine Value of Hypochlorite Solutions with and without Silicate—(Continued).*

Chlorine Value, Grams in 25cc.

Silicate No. 1 Grams	Original	After Warming To 49°C. for 3 hours	Loss of Chlorine Gram	Per Cent
0	0.04175	0.04033	0.00142	2.5
0.5	0.04175	0.04033	0.00142	2.5
3	0.04175	0.04033	0.00142	2.5
		Boiled 20 minutes		
0	0.04000	0.03858	0.00142	3.5
0.5	0.04000	0.03858	0.00142	3.5
1	0.04000	0.03575	0.00425	10.6
3	0.04000	0.03781	0.00319	7.9
5	0.04000	0.03823	0.00177	4.4
		Stood open 1.5 hours		
0	0.04400	0.04224	0.00176	4.0
0.25	0.04400	0.04224	0.00176	4.0
0.5	0.04400	0.04331	0.00069	1.6
1	0.04400	0.04367	0.00033	0.7
3	0.04400	0.04331	0.00069	1.6
5	0.04400	0.04261	0.00139	3.2
		Boiled 1 hour		
0	0.03857	0.03716	0.00141	3.6
0.5	0.03857	0.03680	0.00177	4.5
1	0.03857	0.03716	0.00141	3.6
3	0.03857	0.03680	0.00177	4.5
5	0.03857	0.03645	0.00212	5.5
		Warmed to 38°C. for 2.5 hours		
0	0.03290	0.03115	0.00175	5.3
1	0.03290	0.03115	0.00175	5.3
		38°C. for 2.5 hours		
0	0.11575	0.11257	0.00318	2.7
1	0.11575	0.11257	0.00318	2.7
		Stood open 2.5 days		
0	0.11575	0.08868	0.02707	23.3
1	0.11575	0.09062	0.02613	21.7

Four similar tests gave similar results.

TABLE 106. *Chlorine Value in 5° Baumé Calcium Hypochlorite Solutions in Presence of 10 Grams Unbleached Wood Pulp with and without Silicate.*

		Chlorine Value Remaining	
Hypochlorite Solution Grams		Without Silicate	With 1 Gram Silicate No. 3
32	Open 1 day	None	0.0177
40*	Open 2 days	0.0354	0.1062
40*	Open 2 days	0.0354	0.0708
50	Closed 1 day	0.0088	0.0708
50	Open 1 day	0.0088	0.0880
60	Open 2 days	None	0.0265
40	Open 20 hours	0.0354	0.0531
40	Closed 2 days	0.0177	0.0354

* Different pulps were used in these two tests.

TABLE 107. *Effect of Silicate on Decomposition of Hypochlorite in Presence of Bleached Cellulose.*

Chlorine Value, Grams in 25 cc.

Silicate No. 1 Grams	Original	After Warming to 49°C.	Minutes Warmed	Loss of Chlorine Gram	Per Cent
0	0.19822	0.19043	10	0.00779	3.9
0	0.19822	0.18866	30	0.00956	4.8
0	0.19822	0.18406	60	0.01416	7.1
0	0.19400	0.18692	30	0.00708	3.6
0.5	0.19400	0.18692	30	0.00708	3.6
1	0.19400	0.18833	30	0.00567	2.9
5	0.19400	0.18656	30	0.00744	3.8
10	0.19400	0.18610	30	0.00790	4.7

To 82°C.

0	0.06830	0.05166	10	0.01664	24.3
0	0.06830	0.05166	10	0.01664	24.3
0	0.06830	0.05024	10	0.01806	26.4
0.5	0.06830	0.05343	10	0.01487	21.7
1	0.06830	0.05343	10	0.01487	21.7
2	0.06830	0.05131	10	0.01699	24.8
3	0.06830	0.05237	10	0.01593	23.3
4	0.06830	0.04777	10	0.02053	30.0
5	0.06830	0.05308	10	0.01522	22.2
6	0.06830	0.05267	10	0.01563	22.8
7	0.06830	0.04316	10	0.02514	36.8
8	0.06830	0.05024	10	0.01806	26.4
9	0.06830	0.05308	10	0.01522	22.2
10	0.06830	0.05024	10	0.01806	26.4

In this case the silicious precipitate appears to be the effective agent. Other alkaline earth salts could be substituted with good effect. When less than the full effect of the bleach was secured it was found that the silicate was about equal to 1/3 of the bleach. The results could not be obtained by substituting sodium carbonate for silicate, though sodium hydroxide with calcium hypochlorite gave better colors than calcium hypochlorite alone. The best colors were obtained when silicate was used.[176, 177, 178]

Vincent [179] is of the opinion that the conservation of strength of cotton fabrics bleached with hypochlorite in the presence of silicates is simply a case of the action of alkali. The unstable hypochlorite forms nascent oxygen, the real bleaching agent, according to the following:

$$NaClO + HOH \rightleftharpoons NaOH + HClO$$
$$HClO \rightleftharpoons HCl + (O).$$
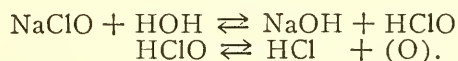
[176] Anon., *Textilechem. Color.*, 633 (May, 1922) ; *Ind. Chimique*, **9**, 407; *C. A.*, **16**, 4354.
[177] Forbes, E., U. S. Pat. 1,401,901 (1921) ; *C. A.*, **16**, 1017.
[178] Polleyn, F., "Dressings and Finishing for Textile Fabrics," London: Scott, Greenwood, **1911**, p. 177.
[179] *J. Phys. Chem.*, **31**, 1310 (1927).

The activity of the solutions is increased by acids and depressed by alkalies so that the silicate would tend to conserve chlorine by keeping it from reacting. The same argument would apply to the observed improvement of fabric strength in the presence of silicate, but would not account for the observation that even though the bleaching reaction may be less the color attained is better. Evidently the silica has some part in this phenomenon, which is, after all, the one of industrial importance. If the bleacher can use less chlorine, reduce the loss of fiber strength, and at the same time obtain a better white, he has gained on three counts. Vincent postulates a gain in strength due to silica adsorbed on the fibers, which needs proving.

The increase of ash is very small in the first few treatments and the increase of strength is marked. It might be due to a mercerizing action. Further, the character of silica deposited on the fiber as a hydrous, amorphous, and tenuous layer is not such as to lead one to expect it to cause an appreciable effect on strength. The differences in strength with and without silicate increase with the number of treatments both in detergent and bleaching experiments as the amount of silica retained also gains, but the concept of a protective action of silica seems more tenable than the idea of silica's adding much strength to cotton fibers. The strength of papers may indeed be improved by silicious deposits, but this is probably a cementing action.

Vincent showed the improved color of fabrics bleached with hypochlorite in the presence of silicate to be due to the more ready removal of colored material, not identified, which appears to be a by-product of the bleaching. This may be due to a protective action, which prevents its adsorption or absorption during bleaching which would be expected if the silica were deposited as a film. He says this is unquestionably an advantage and sufficient reason for adding silicate to bleaching solutions.

SILICATES IN DETERGENT PRACTICE.

SILICATES ALONE.

Overall Washing. Silicate solutions alone have a limited use in cleansing operations. They are suitable for reclaiming oily cotton waste of the sort employed for cleaning machinery. Mechanics' overalls and other very dirty textiles are well cleaned with $Na_2O, 3.3SiO_2$ to $Na_2O,4SiO_2$ in hot solutions containing about 2 per cent solids.[180-183]

[180] *Neueste Erfindungen u. Erfahrungen*, **2**, 69 (1875).
[181] Stericker, Wm., *Ind. Eng. Chem.*, **15**, No. 3, 244 (1923).
[182] Meyer, R., *Dingler's Polyt. J.*, **227**, 280-289 (1878) ; *Chem. Zentr.*, **9**, 281-282; *J. Chem. Soc.*, **34**, A, 534-535 (1878).
[183] Kunheim, L., *Polyt. Centralblatt*, 414 (1857) ; *Chem. Zentr.*, **28**, 288.

Metal Cleaning. For vigorous detergent action where there is no risk of damage to the material cleansed, as in preparing metals for plating or enameling, sodium metasilicate is useful.[184] Staley [185] used a more silicious silicate and rated it below trisodium phosphate (Na_3PO_4) without considering whether other silicates would or would not fall into the same relative position. This is a good example of the risk of ignoring the great differences between silicates of different composition.

De-inking Printed Paper. The removal of printers' ink from paper without attack upon mechanical wood pulp, so that white paper may be made from waste, can be accomplished with $Na_2O, 3.3SiO_2$ in a solution of less than 1 per cent, either hot or cold.[186-189] The paper is pulped, soaked in the silicate, washed, and remade into paper. The pigment is deflocculated and washed away. Stronger reagents can be used on paper made from chemical pulp.

The effect of silicate ratio on de-inking of paper was studied by Briggs and Rhodes,[190] who proposed their technic of measuring color of the de-inked paper as an index of detergent power. This requires the assumption that ink is a typical dirt, to which the present writer cannot assent and while a more representative material might be substituted it would be very difficult to standardize all the variables to a satisfactory degree.

Their comparison of de-inking reagents shows silicate solutions to be effective and suggests the degrees in which other materials approach the detergent action of soap. It should be noted that a suspension of fullers' earth in sodium hydroxide solution contains sodium silicate.

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[184] See also: Hutchins, Nancy A., U. S. Pat. 930,965 (Aug. 10, 1909).
[185] Staley, H. F., *The Ceramist,* **6**, 554-560 (1925) ; *Ceram. Abstracts,* **4**. 332.
[186] Jespersen, T., U. S. Pat. 1,424,411 (Aug. 1, 1922) ; *C. A.,* **16**, 3394; *cf. Paper,* **35**, 510.
[187] Stutzke, R. W. G., U. S. Pat. 1,545,707 (July 14, 1925).
[188] Henkel, Hugo, and Otto Gessler, U. S. Pat. 988,874 (April 4, 1911).
[189] Bancroft, W. D., *Chem. & Met. Eng.,* **23**, 454-456 (1920).
[190] *Colloid Symposium Monograph,* New York: Chemical Catalog Co., **4**, 311 (1926).

TABLE 108. *Comparison of Detergents.*

50 grams of printed paper pulped 30-40 minutes in 1 liter of solution.
Pulped, washed.

Pulping Solution	Concentration	White-ness	Apparent De-Inking (Per Cent)
Sodium oleate	5 grams per liter	0.79_5	100
Fullers' earth in 0.02N NaOH	10 grams per liter	0.76_4	95
Sodium silicate, "O," Na$_2$O 3.3Si$_2$O, 1.39 specific gravity	0.1N	0.72_1	84
Sodium resinate	5 grams per liter	0.71_7	83
Sodium hydroxide	0.1N	0.71_5	82
Sodium hydroxide	0.02N	0.70_0	78
Borax	0.1N	0.69_3	75
Gelatin in 0.02N NaOH	10 grams per liter	0.68_3	71
Sodium hydroxide (70°-55°)	0.02N	0.68_0	70
Sodium carbonate	0.1N	0.67_8	69
Gum arabic	10 grams per liter	0.66_8	65
Gelatin	10 grams per liter	0.64_4	55
Sucrose	0.1N	0.62_8	46
Distilled water	....	0.60_3	30
Egg albumen	10 grams per liter	0.59_7	26
Sodium chloride	0.01N	0.56_7	0
Calcium chloride	0.01N	0.56_0	0
Aluminum chloride	0.01N	0.55_0	0
Calcium hydroxide	(Saturated)	0.55_6	0

The comparison of three commercial ratios did not show a marked superiority of any one.

TABLE 109. *De-Inking with Sodium Silicate.*

10 grams paper pulped 30 min. Pulped, washed in water.

Concentration Equivalents Na$_2$O per Liter	Whiteness "S" Brand SiO$_2$: Na$_2$O=3.89	"O" Brand SiO$_2$: Na$_2$O=3.23	"C" Brand SiO$_2$: Na$_2$O=2.0
0.2	0.69_5	....	0.63_0
0.1	0.73_0	0.72_3	0.70_0
0.05	0.71_4	0.71_2	....
0.02	0.69_0	0.69_0	0.69_0

SILICATES IN CONJUNCTION WITH OTHER MATERIALS.

Sodium Hydroxide. Kier boiling of cotton is done with sodium hydroxide as the primary reagent. Five per cent on the weight of the goods is usual. Up to 1 per cent of Na$_2$O, 3.3SiO$_2$, because it assists emulsification and prevents rust stains, has found place in commercial practice. More alkaline silicates are also used.[191, 192]

Sodium Chloride. Sodium chloride added to silicate solutions has the property of flocculating grease and insoluble dirt to a degree which

[191] Beltzer, F. J. G., *Rev. génér. chim.*, **12**, 285-298 (1909); *Chem. Zentr.*, **80**, 1597; *C. A.*, **4**, 237-238.
[192] Trotman and Thorp, "The Principles of Bleaching and Finishing Cotton," Philadelphia, Pa.: Lippincott, **1911**, p. 109.

makes it useful as a rough test for following the progress of a washing operation. A measured amount of wash liquor is treated with salt brine, centrifuged, and the volume of precipitate taken as an index.[193] Salt also has the property of preventing the adherence of oily dirt to metal surfaces, as the buttons of overalls, or the drums or shells of metal washing machines. Very satisfactory cleansing of overalls was obtained as follows: [194]

> 1st bath—Cold rinse in 8 inches water (with load) 5 min.
> 2nd bath—8 inches water 82°C., 4.53 kilograms (10 pounds) silicate
>   of soda and 4.53 kilograms sodium chloride, 15 min.
> 3rd bath—10 inches water 82°C., 3 min.
> 4th bath—Repeat second bath.
> Enough 5-min. hot rinses until last rinse comes clear from wash
>   wheel.
> This formula is used in a 36 x 54 wheel, 50 overalls to the load.

The single objection to this method lies in the labor required to polish metal parts of machinery on which this solution has dried before rinsing.

The same idea is of use in making platers' cleaning solutions. Sodium metasilicate and salt will remove obstinate grease films and leave surfaces in condition to receive films of electro-deposited metals or of paint.

Sodium Carbonate. Since 1876 mixtures of sodium carbonate and silicate have been on the market as detergents.[195] In Germany, the name "Bleichsoda" (bleaching soda) is applied. It antedates any washing powder containing active oxygen or chlorine and depends upon the fact that it prevents discoloration from rust and has a gradual whitening effect on fabrics resulting from the action, not yet fully explained, of colloidal silica.[195-200] A typical material of this sort is a powder containing the following:

> 23 per cent $Na_2O, 3.4SiO_2$, 1.35 specific gravity (38° Baumé)
> 57 per cent $Na_2CO_3.10H_2O$
> 20 per cent Na_2CO_3

Aluminum Oxide. Since colloidal properties are recognized as helpful in detergent operations, the idea that the ability to act as a mordant

[193] Wakefield, citation in *Silicate P's & Q's*, **5**, No. 6 (1925), Philadelphia, Pa.: Philadelphia Quartz Company.

[194] Schupp, Arthur F., *Am. Inst. of Laundr., Quarterly*, 26 (October 15, 1924).

[195] Bailey, Broadus, U. S. Pat. 1,635,244 (July 12, 1927).

[196] Welter, A., Brit. Pat. 136,841 (Dec. 18, 1919) ; *C. A.*, **14**, 1416.

[197] Mayer, "Das Wasserglas," 33, Friedr. Vieweg & Sohn Akt.-Ges., Braunschweig (1925).

[198] Geisenheimer, G., *Compt. rend.*, **118**, 192-194 (1894) ; abstracts in *J. Chem. Soc.*, **66**, 189; *Chem. Zentr.*, **65**, 456; *J. Soc. Chem. Ind.*, **13**, 727; *Chem. News*, **69**, 69.

[199] Beltzer, F. J. G., *Rev. chim. ind.*, **21**, 233-238 (1910) ; *C. A.*, **4**, 2982-2983 (1910).

[200] Kühl, H., *Seifensieder Ztg.*, **45**, 459 (1918).

could be added to a carbonate-silicate mixture by introducing aluminates, which also yield colloidal solutions, is attractive. These compounds have found a rather limited place in laundering because they are more costly and have little advantage over the mixtures which contain carbonate and silicate only. The loss of strength in cotton, wool, and silk is said to be less than with sodium carbonate, which is also true of the carbonate and silicate mixtures.[201-204] The aluminous compound from a 5 per cent solution did not injure the goods when they were ironed without rinsing. Special merits claimed for various silicate mixtures would outrun the scope of the present treatise, it is obvious that many permutations of detergent substances may be useful.[205-207]

SILICATES AND SOAPS.

Historical. Thus far we have considered silicated washing reagents from the viewpoint of detergent action. This is fundamentally sound, but the maker of soaps must consider also their appearance and the conditions of their manufacture. Sheridan [208] took out the first patent for a silicated soap in 1835. Thomas followed in 1856,[209] but in this country it was not until the period of the Civil War, 1861-1865, that the practice assumed any considerable importance. At that time the supply of rosin from the southern states was shut off from northern soap factories, which, together with high prices and general shortage of fats, induced the use of silicates to extend the available supply.

When there was no longer a shortage, the use of silicates in soap continued in vogue and the total amount steadily increased until again during the World War the necessity of conserving fats as comestibles, particularly in central Europe, caused a larger reliance on silicates for detergent work. Upon the return of peace the experience gained during the emergency gave the silicated washing materials a still stronger foothold and they are to-day accepted by the public with great

[201] Kayser, Adolf, Brit. Pat. 6934 (March 23, 1909).
[202] Guernsey, F. H., U. S. Pat. 1,419,625 (June 13, 1923); *C. A.,* **16,** 2761; Brit. Pat. 200,175 (July 4, 1923).
[203] Cowles, U. S. Pat. 1,445,004 (Feb. 13, 1923).
[204] Guernsey, F. H., *Am. Dyestuff Rep.,* **12,** 176-181, 208, 217-218, 277-280, 438-439, 496-497, 563-570 (1923).
[205] Marcus, Robt., Ger. Pat. 322,088 (Aug. 22, 1917): *C. A.,* **15,** 2160.
[206] Ewe, Geo. E., *Pract. Drug.* **41,** No. 3, 22-23 (1923); *C. A.,* **17,** 1861.
[207] Barlocher, Otto, Ger. Pat. 318,151 (May 4, 1918); *C. A.,* **15,** 1974; Ger. Pat. 314,909; *C. A.,* **15,** 1974.
[208] Sheridan, Joseph Charles, Brit. Pat. 6894 (1835).
[209] Simmons, Wm. H., "Soap, Its Composition, Manufacture, and Properties," p. 66, London: Pitman, **1917.**

freedom when offered side by side with soaps which contain no silicate.[210-214]

Boiled Soap. When soap has been finished by boiling with successive changes of alkali and separated from the liquors containing the glycerin, it is usually delivered to a mixing device called a crutcher which assures its homogeneity. While the soap is hot and viscous and under agitation of a heavy stirring device, the silicate is put in. The first effect is to thin the soap, but if the amount and quality are appropriate to the soap in question, and the temperature is right, an unctuous texture develops quickly and the soap is smoother than before.

As soap and silicate are not miscible in all proportions, it is necessary
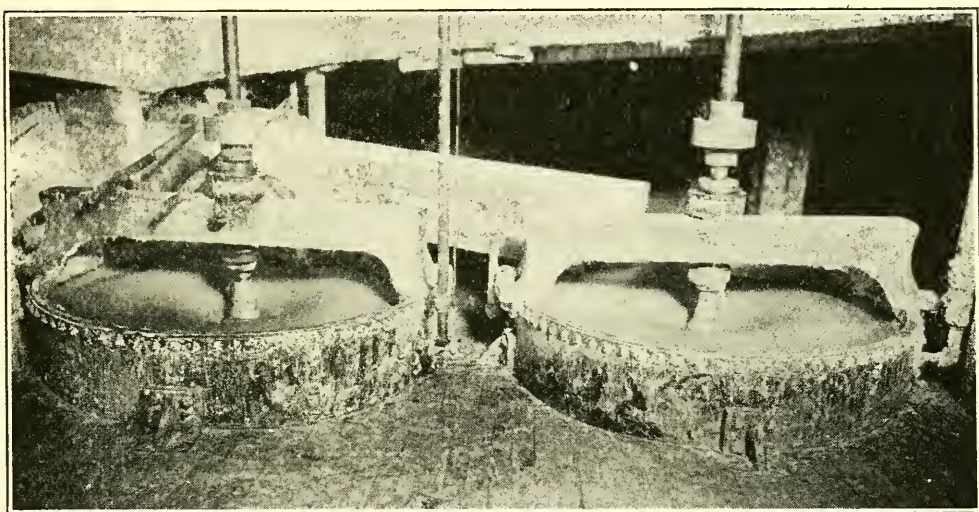
Fig. 162.—Crutching Silicate into Soap (Top View).

to have regard to several factors in adding silicate. In general, softer fats yield soaps which will carry less silicate. Hydrogenated oils carry less than tallow. The more silicious silicates are able to take up alkali from the soap colloid and this may lead to a grainy condition in which soap and silicate are separated, a part of the silicate in the continuous phase. This condition may be obviated by proper selection of the grease stock on the one hand—harder stock for highly silicated soaps—and on the other, by adjustment of alkali. $Na_2O,2SiO_2$ in solution mixes freely

[210] G. E. J., *Seifenfabr.,* **39**, 253-256 (1919); *C. A.,* **13**, 2770.
[211] Guillin, R., Report of lab., Soc. des Agriculteurs (France: 1917-8); Bull., Soc. des Agriculteurs (France: 1919); *C. A.,* **13**, 2409.
[212] P. L., *Seifensieder Ztg.,* **49**, 623-624; *C. A.,* **17**, 1160; *Oil Colour Trade J.,* 1221 (1922).
[213] Mayer, *loc. cit.,* **3**.
[214] *Seifensieder Ztg.,* **29**, 775 (1908).

with a well saponified stock. Many soapmakers practice the addition of varying amounts of sodium hydroxide to silicate of the approximate composition $Na_2O, 3.3SiO_2$ in order to make smoother mixtures.[215, 216] These generally work out to an amount of sodium hydroxide less than that required to bring the ratio to $Na_2O, 2SiO_2$. The relatively stable
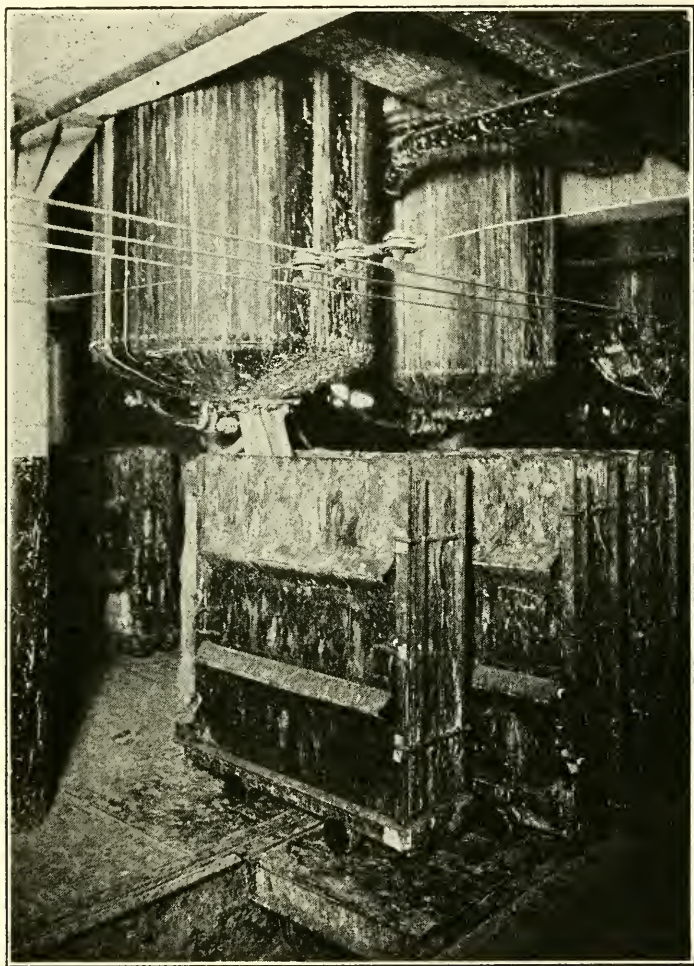
Fig. 163.—Drawing Hot Silicated Soap from Crutchers into Frames. Same apparatus as foregoing picture.

behavior of $Na_2O, 2SiO_2$ when mixed with soap suggests the presence of sodium disilicate or possibly $NaHSiO_3$ in which the alkali-silica ratio is the same. It should be pointed out that a considerable time after mixing is necessary for the silicate-caustic solution to come to equilibrium and, as indicated in discussing the constitution of silicate solutions

[215] Gathmann, H., "American Soaps," Chicago: Gathmann, **1893**, p. 72, **187**, 214, 236.
[216] Leimdörfer, J., *Kolloidchem. Beihefte*, **2**, 343-398 (1911).

(Chapter II), it is not proven that, even then, the solution is identical with one made by dissolving glass of the same ratio.

The concentrations at which silicate is added to soap vary widely; $Na_2O,2SiO_2$ may be put in as a viscous liquid at 1.7 specific gravity, and lower concentrations of this and the more silicious types of silicate are employed according to the final result desired.

The amounts put into twenty brands of laundry soap sold on the
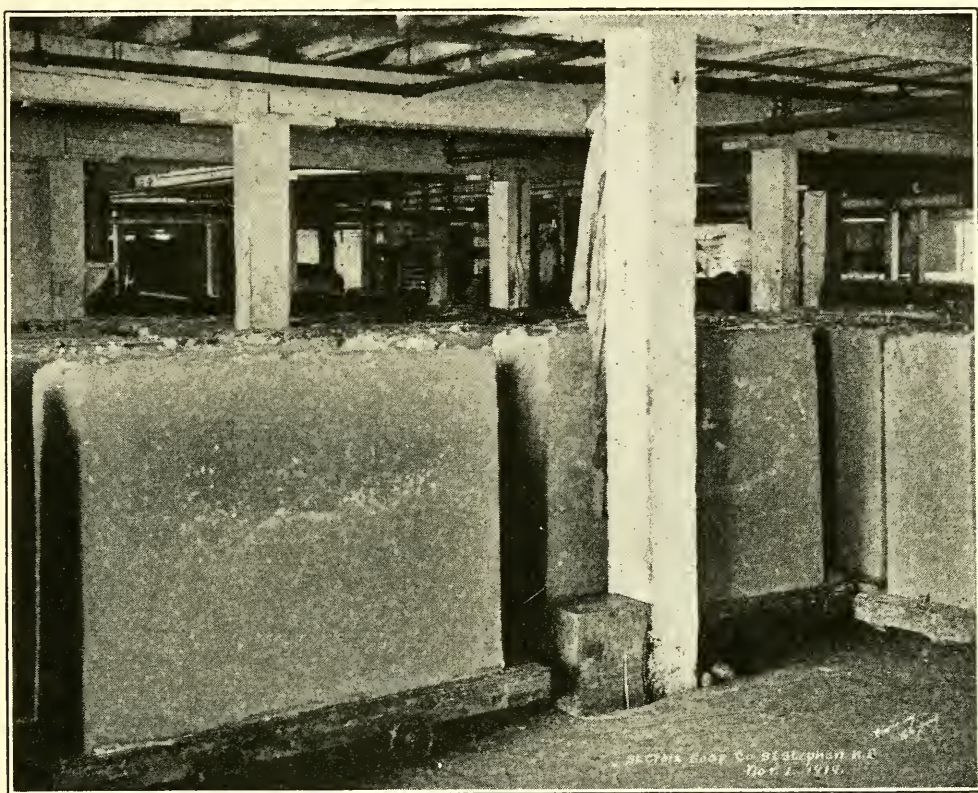
Fig. 164.—Silicated Soap after Removal of Frames.

American market in 1922 averaged 11.86 per cent anhydrous silicate in the finished soap and ranged from 1 to nearly 25 per cent.[217]

After soap and silicate have been well incorporated in the crutcher the mass is run into frames to cool, as shown in the illustration. Here separation may take place if the mixture is unstable. To avoid this it is well to let the soap leave the crutcher at as low a temperature as is consistent with clearing the apparatus, and to cool the frames as rapidly as convenient. The frames should also be taken at once to a place where they can remain undisturbed till the soap has fully set and the sides can be stripped off ready for cutting into bars and cakes. Devices

[217] Federal Trade Com. vs. Procter and Gamble, Docket 852, Exhibit No. 16.

which chill the hot soap by refrigeration so that it solidifies in a few minutes are applicable to silicated soaps.[218-246]

Cold Made Soaps. Although a large proportion of commercial soap is made by boiling with sodium hydroxide solutions and salting out the soap curd, other methods are also compatible with the use of silicates.

[218] Storer, F., *Chem. News,* **8,** 17 (1863) ; *Répertoire de chimie appliqué,* **5,** 5-7 ; *Poly. J.,* **168,** ser. 4, 18, 463-464.

[219] *Poly. J.,* **178,** 416 (1865) ; *Chem. Zentr.,* **37,** n.s., **11,** pt. 1, 559-560 (1866).

[220] Schnitzer, Guido, *Poly. J.,* **203,** ser. 5, **3,** 129-132 (1872) ; *Le Moniteur scientifique,* **14,** ser. 3, **2,** 350-352 (1872) ; *J. Chem. Soc.,* **25,** 10, 340 (1872).

[221] Droux, M. S., *Am. Chem.,* **4,** 438 (1874).

[222] Kingzett, Charles Thomas, "History, Products and Processes of the Alkali Trade," Longmans, **1877,** p. 175-177.

[223] Muspratt, James Sheridan, "Encyclopedia of Chemistry," **2,** Philadelphia, Pa. : Lippincott, **1877-80,** 779-780.

[224] Artus, Willibald, "Grundzüge der Chemie in ihrer Anwendung auf das praktische Leben," **64,** Wien : Hartleben's chemisch-technische Bibliothek, **1880,** p. 247-248.

[225] *Pro. Am. Pharm. Ass.,* **31,** 68 (1883).

[226] Brannt, William T., "Practical Treatise on the Manufacture of Soap and Candles," Baird, **1888,** 218-219, 382-385, 408-409, 421-422.

[227] Engelhardt, Alwin, "Handbuch der praktischen Toiletteseifen-Fabrikation," **163,** Wien : Hartleben's chemisch-technische Bibliothek, **1888,** 109-110.

[228] Gadd, W. Lawrence, "Soap Manufacture," G. Bell, Technological handbooks, **1893,** p. 106-112.

[229] Carpenter, William Lant, "Treatise on the Manufacture of Soap and Candles, Lubricants and Glycerin" (2nd ed., E. & F. N. Spon, **1895**), 143-145, 198-200.

[230] Engelhardt, Alwin, "Handbuch der praktischen Toiletteseifen-Fabrikation," **136, 137,** Wien : Hartleben's chemisch-technische Bibliothek, **1896,** 49-50, 350-351, 185-187.

[231] Cameron, James, "Soaps and Candles," 2nd ed., Churchill, **1896,** 27-31, 111-115.

[232] Hurst, George H., "Soaps ; a Practical Manual of the Manufacture," London : Scott, Greenwood, **1898,** 47-49, 243-244, 309-311, 342-344, 359-360.

[233] Bach, Karl, *Neueste Erfindungen und Erfahrungen,* **29,** 81 (1902).

[234] International Correspondence Schools, Scranton, Pa., Chem. Tech., **3,** International library of technology, **18-20,** 2 ser. 44, 3-5 (1902).

[235] Andés, Louis Edgar, *Neueste Erfindungen und Erfahrungen,* **30,** 100-102 (1903) ; "Praktisches Rezeptbuch für die gesamte Fett-, Öl-, Seifen- und Schmiermittel-Industrie," Wien : Hartleben's chemisch-technische Bibliothek, **1909,** 56-88, 186-190.

[236] Stiepel, C., *Seifenfabr.,* **24,** 225-227 ; *Chem. Zentr.,* **75,** 1, 1112 (1904).

[237] Ubbelohde, Leo, "Handbuch der Chemie und Technologie der Öle und Fette," 1-3, pt. 2, Leipzig : Hirzel, **1911,** 592-596.

[238] *Z. angew. Chemie,* **21,** pt. 1, 1025 (1908).

[239] Peter, Julius, *Z. angew. Chemie,* **26,** pt. 2, 138 (1913).

[240] Schmidt, R., *Z. angew. Chemie,* **26,** pt. 2, 311 (1913).

[241] Simmons, William H., "Soap ; Its Manufacture, Composition, and Properties," London : Pitman, **1917,** 25-26, 66.

[242] Lamborn, L. L., "Modern Soaps, Candles, and Glycerin," 3rd ed., New York : D. Van Nostrand & Co., **1918,** 115-118.

[243] Schuck, E., *Am. Perfumer,* **14,** 355-356 (1919) ; *C. A.,* **14,** 854.

[244] Wiltner, Friedrich, "Die Fabrikation der Toilettseifen und der Seifenspezialitäten," 3rd ed., Wien : Hartleben's chemisch-technische Bibliothek, **1920,** 179-180.

[245] Wright, Charles Romley Alder, "Animal and Vegetable Fixed Oils," 3rd ed., Griffin, **1921,** 834-835.

[246] Deite, Carl, "Handbuch der Seifenfabrikation," 5th ed., Berlin : Springer, **1921.**

So-called cold soaps, in which all the products of reaction are included in the cake, have a limited use and have long been made with silicate. Typical formulas are the following:

33.98 kilograms	(75	pounds)	tallow
11.33 "	(25	")	coconut oil
33.98 "	(75	")	caustic soda 35.5°Baumé
56.63 "	(125	")	Na₂O, 3.34SiO₂, 41°Baumé
9.06 "	(20	")	potassium carbonate sol. 36°Baumé

144.98 kilograms (320 pounds) Soap

33.98 kilograms	(75	pounds)	tallow
11.33 "	(25	")	coconut oil
31.71 "	(70	")	caustic soda 35.5°Baumé
45.3 "	(100	")	Na₂O, 3.34SiO₂, 41°Baumé
7.70 "	(17	")	potassium carbonate 36°Baumé

130.02 " (287 ") soap

Refined cottonseed oil up to 30 to 50 per cent can be substituted for an equal weight of tallow, if the tallow is hard. If the tallow is soft or mixed with grease, less oil should be used. The soap will not be quite so hard and will take longer to harden, but it will be a good washing soap. In these formulas the amounts of caustic are calculated so as to include the proper excess for the silicate to take up.

Potassium carbonate is used in these soaps to improve texture and solubility. Sodium carbonate can be substituted at the cost of less attractive appearance.

Fatty acids are also directly saponified with sodium carbonate or silicate or mixtures of these. This method is advantageous where soaps are to be highly silicated and the amount of water which is necessarily present in the curd soap plus the amount introduced by the silicate is too great to yield a cake of satisfactory texture.[247] The fatty acids can be saponified in the presence of relatively small amounts of water and by their aid a cake containing a large amount of silicate can be made without the need of a drying process, which would too greatly increase the cost of laundry bar soaps. Numerous formulas have been proposed, of which the references given below may be taken as typical.[248-254]

[247] Blasweiler, T. E., Ger. Pat. 320,829 (April 11, 1919) ; *C. A.*, **15**, 2009.
[248] Lara, F., U. S. Pat. 1,335,246 (March 30, 1920) ; *C. A.*, **14**, 1616.
[249] Pech, P. L. E., U. S. Pat. 1,462,243 (July 17, 1924) ; *C. A.*, **17**, 3108.
[250] Shields, Fred W., U. S. Pat. 1,481,811 (Jan. 29, 1924) ; *Soap Gazette*, **26**, 134.
[251] Reinfurth, N., Brit. Pats. 146,223 and 146,224 (June 26, 1920) ; *C. A.*, **14**, 3541.
[252] Stiepel, C., *Seifenfabr.*, **24**, 225-227; *Chem. Zentr.*, **75**, 1, 1112 (1904).
[253] Berge, *Seifensieder Ztg.*, **47**, 641-643 (1920) ; *C. A.*, **14**, 3809-3810.
[254] Kalle and Company, Ger. Pat. 381,108.

Result of Use of Silicate. Though silicate makes soap softer up to the time of setting, it makes a firmer finished cake.[255-257] Silicated soaps are apt to contain more water than the same stocks without silicate. Silicates cause gelation of sodium and potassium oleates in lower dilution than sodium carbonate.

TABLE 110. *Sodium Oleate and Sodium Silicate.*
(Fischer)

Concentration of Mixture	Remarks
5cc. m sodium oleate + 9cc. H₂O + 1cc. m/2 sodium silicate	Mobile liquid
5cc. " " " + 8cc. " + 2cc. " " "	Less mobile liquid
5cc. " " " + 7cc. " + 3cc. " " "	Viscid
5cc. " " " + 6cc. " + 4cc. " " "	Very viscid
5cc. " " " + 5cc. " + 5cc. " " "	Solid gel
5cc. " " " + 4cc. " + 6cc. " " "	Solid gel
5cc. " " " + 3cc. " + 7cc. " " "	Beginning separation
5cc. " " " + 2cc. " + 8cc. " " "	Great dehydration and separation
5cc. " " " + 1cc. " + 9cc. " " "	Great dehydration and separation
5cc. " " " +10cc. m/2 sodium silicate	Great dehydration and separation
5cc. " " " +10cc. H₂O (control)	Mobile liquid

TABLE 111. *Potassium Oleate and Sodium Silicate.*
(Fischer)

Concentration of Mixture	Remarks
5cc. m potassium oleate + 9cc. H₂O + 1cc. m/2 sodium silicate	Mobile liquid
5cc. " " " + 8cc. " + 2cc. " " "	Mobile liquid
5cc. " " " + 7cc. " + 3cc. " " "	Mobile liquid
5cc. " " " + 6cc. " + 4cc. " " "	Mobile liquid
5cc. " " " + 5cc. " + 5cc. " " "	Viscid liquid
5cc. " " " + 4cc. " + 6cc. " " "	Viscid liquid
5cc. " " " + 3cc. " + 7cc. " " "	Viscid liquid
5cc. " " " + 2cc. " + 8cc. " " "	Solid gel
5cc. " " " + 1cc. " + 9cc. " " "	Solid gel
5cc. " " " +10cc. m/2 sodium silicate	Viscid liquid
5cc. " " " +10cc. H₂O (control)	Mobile liquid

As the soap dries it becomes harder and less soluble so that very old samples of highly silicated soaps are hard to dissolve in cold water and if wetted and dried at intervals of a few days the cake tends to be covered with a hard silicious film, but this is only evident in the soaps containing the higher amount, and in any case does not appear when a piece is completely dissolved at one operation, as in the family wash.

The use of solutions containing silicate and sodium hydroxide which

[255] Fischer, M. H., "Soaps and Proteins," New York: Wiley, **1921**, 194 *et seq.*
[256] Fischer, M. H., and G. D. McLaughlin, *Kolloidchem.*, **15**, 1-102; **16**, 99-133, 134, 175179 (1922); *C. A.*, **17**, 25.
[257] Lederer, E. L., *Z. angew. Chem.*, **37**, 637 (1924).

have not reacted fully leads to a final product which irritates the hands in use and is more likely to be disfigured with a white efflorescence of sodium carbonate. Simmons [258] describes the use of $Na_2O,2SiO_2$ and says that it reduces the tendency of sodium carbonate, even when added
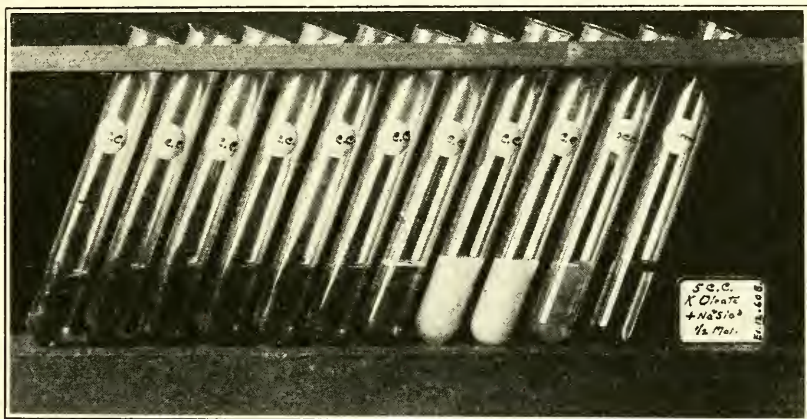
Fig. 165.—Addition of Silicate to Potassium Oleate.

as such, to appear as a bloom on the surface of soap, while McBain speaks of silicated soaps as especially likely to form carbonate on exposure to the air—differences which may easily be due to the type of silicate and the manner of its introduction into soap.[259]
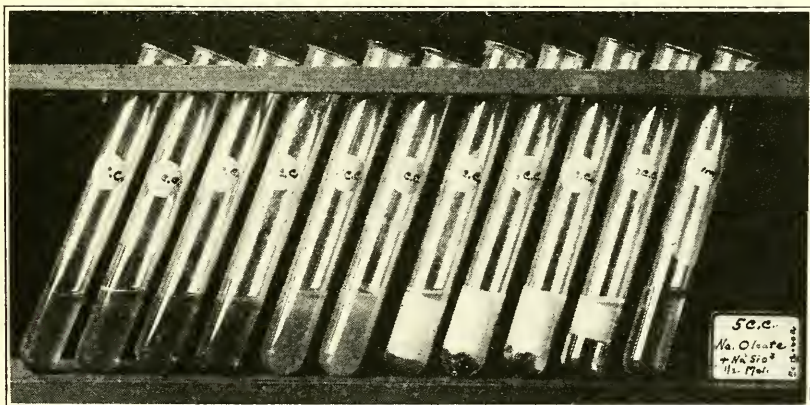
Fig. 166.—Addition of Silicate to Sodium Oleate.

Leimdörfer considers that the prevention of efflorescence by silicate on a soap which had contained free alkali is a matter of adsorption of sodium hydroxide on silica. When the capacity of silica to adsorb is

[258] Simmons, W. H., "Soap, Its Composition, Manufacture, and Properties," London: Pitman, 1917, 66.

[259] 4th Colloid Report, Sci. Ind. Research, London: His Majesty's Stationery Office, 1922, 244-263.

exceeded the bloom reappears and when there is not enough alkali the silicate coagulates the soap and efflorescence may again take place.[260]

The silicate-soap complex has an emulsoid character which is largely affected by the viscosity of the two phases, particularly the continuous one. Fischer points out that the hydration, which causes the soap to stiffen, is a process which requires considerable time. Following this lead he was able to add water to silicate soap mixtures which had separated, wait until the water had been taken up and then work the mass into new batches of soap which were smooth and satisfactory. The opinion is here offered that the efflorescence of silicate-soap mix-- tures is more dependent upon whether the system is a well hydrated and fine grained emulsion than upon any exact relation between Na_2O and SiO_2. This is supported by the fact that the white silicated soaps now popular in America are made with silicates which, according to the older teaching, should be impossible. Yet they are smooth and show little tendency to bloom. Silicates, like other electrolytes, can salt soap out of solution but the satisfactory mixture is an emulsion of two viscous hydrophile colloids in which most of the silicate is a finely dispersed phase. When the emulsion is relatively gross the silicate characteristics are more in evidence. The ability to control the efflorescence of added carbonate is primarily a matter of including it in a viscous, highly dispersed vehicle.

In America the practice of using the silicates with more than two mols of silica is widespread. The soap is finished slightly alkaline in the boiling kettle and the silicate, $Na_2O, 3.3SiO_2$, or somewhat more alkaline, is used to take up the free alkali.[261]

Silicates reduce the tendency of soaps containing rosin to be sticky. They improve texture and gloss and tend to increase the translucent appearance of soap.[262]

Much of the older literature refers to soluble silicates in soaps as fillers.[263] The distinction between inert materials added to soap and those which assist detergent action has [264-266] been aptly recognized by the U. S. Bureau of Standards [267] in the use of the term "builders"

[260] *Kolloidchem.,* **2,** 343-398 (1911).

[261] Edeler, A., *Ind. Eng. Chem.,* **17,** 196 (1925).

[262] Weber, K. L., *Seifensieder Ztg.,* **49,** 458-460, 479-481, 494-495 (1922) ; *C. A.,* **16,** 3224.

[263] *Seifenfabricant,* No. 15 (1885) ; *Chem. Zentr.,* **16,** 967-968 (1885).

[264] Artus, *Dingler's poly. J.,* **178,** 416; *Chem. Zentr.,* **37,** 559-560 (1866).

[265] Andés, L. E., "Wasch-, Bleich-, Blau Stärke- und Glanzmittel," Hartleben's Chemisch-techniche Bibliothek, Wien, **1909.**

[266] *Dingler's poly. J.,* **222,** ser. 5, **22,** 501 (1876) ; *Chem. Zentr.,* **56,** ser. 3, **16,** 956-957 (1885).

[267] *Bur. of Standards Circ.* No. 62, 3rd ed., 1-24 (1923).

and in specifications calling for a hard-water laundry soap containing up to 20 per cent matter insoluble in alcohol.

In view of the foregoing, it will be seen that the question of whether the use of silicates in soap constitutes adulteration or no, becomes highly technical. Silicates are not soap; mixtures of silicate and soap, or either of them separately, are useful washing agents. Silicates are cheaper than soap and this fact should be taken into account in setting the price of mixtures. A case before the Federal Trade Commission in which this point was raised ended by the withdrawal of that part of the complaint concerning silicates. The testimony showed that the largest tonnage of soap sold in the competitive marked in the United States is made up of the silicated brands.[268]

Silicates also have their place in chip soaps and soap powders, where their function is not essentially different from that in cake soaps.[269-271]

Specific formulas might be multiplied at length, but they are on record for those who are specially interested and they do not add greatly to our understanding of the nature of silicate solutions.

Small amounts of $Na_2O, 3.3SiO_2$ in soap prevent free fats from becoming rancid on storage. Additions of 1 per cent of a 1.38 specific gravity solution are sufficient. The nature of the action has not been explained, but it evidently has to do with free fatty acids and experience indicates that colloidal silica has an active part because like quantities of other alkalies including sodium carbonate are less able to keep the soap sweet. Sodium hydroxide is effective until it is carbonated, and the value of silicate may have to do with its ability to prevent decomposition by carbon dioxide of the air to the less potent carbonate. There is thus a function for silicate in soaps in which its detergent properties are not involved. The amounts needed are small. It is permissible to use them in toilet soaps or those designed for the most delicate uses. In fact the practice of adding small quantities of silicate to shaving creams and alkaline cosmetics, to permit the use of aluminum containers which would otherwise be attacked, indicates that the mixture containing silica is milder than the original product.

ANALYSIS OF DETERGENTS CONTAINING SOLUBLE SILICATES.

Separation of Soap and Silicate. The basis of separation between soap and soluble silicate is the insolubility of the latter in alcohol. It

[268] Federal Trade Com. vs. Procter & Gamble, *loc. cit.*

[269] St. D., *Chemisches Repertorium*, **29**, 11, 400 (1905); *Seifensieder Ztg.*, **32**, 814.

[270] Steffan, M. O., *Seifensieder Ztg.*, **48**, 589-591, 612-614, 631-632 (1921); *C. A.*, **15**, 376.

[271] Siebel, R., *Z. deut. Öl-Fett-Ind.*, **45**, 739-741 (1925); *C. A.*, **20**, 999.

is necessary that the moisture content of the soap should be low and that there be little water in the alcohol. The U. S. Bureau of Standards [272] recommends 94 per cent at least. A 10 gram sample after digesting, hot, with 200 cc. neutral alcohol is filtered on a tared filter, washed with hot alcohol, and dried on a tared filter at 100° to 105°C. for 3 hours. This residue includes sodium silicate, sodium carbonate, and sodium borate. The other salts may be determined by well known methods of analysis, but the interpretation of the results respecting silicate is difficult. In the first place, the precipitate is not completely dehydrated at 105°C. in 3 hours, and secondly the ratio between Na_2O and SiO_2 is usually different from the silicate solution put into the soap. As all the soluble silica is in the precipitate it is best to determine it and then to calculate back to the silicate known or assumed to have been added to the soap. If there is no material insoluble in water the original soap may be charred for the determination of silica. There is no analytical method available for determining how much of the sodium oxide in a soap of unknown history was introduced as silicate.

Determination of Free Alkali. Determination of free alkali in the presence of silicate also requires some interpretation. Edeler [273] determined free alkali in the alcoholic extract of silicate solutions alone and mixtures of silicate solutions with neutral alcoholic soap, with the

TABLE 112. *Titrations of Alcoholic Filtrates from Silicated Soaps.*

Free Na_2O in Soap Before Adding Silicate, Per Cent	Resulting Ratio Na_2O, SiO_2 (Molecular)	Cc. N H_2SO_4 to Neutralize Alcoholic Filtrate *		Apparent Free Na_2O in Silicated Soap, Per Cent
0.0	1 : 3.22	0.05	0.05	0.01
1.21	1 : 2.54	0.30	0.40	0.07
2.32	1 : 2.12	0.50	0.50	0.10
5.02	1 : 1.52	2.40	2.60	0.52

* Each analysis was made in duplicate on separate samples.

TABLE 113. *Titrations of Alcoholic Filtrate from Sodium Silicates of Varying Composition.*

NaO_2 Per Cent	SiO_2 Per Cent	Ratio $NaO : SiO_2$ (Molecular)	Cc. N H_2SO_4 Neutralize Alcoholic Filtrate			
			Soap Absent		Soap Present	
			(1)	(2)	(1)	(2)
9.18	29.71	1 : 3.33	0.10	0.10	tr	tr
11.37	28.18	1 : 2.55	0.25	0.25	0.05	0.05
13.48	26.13	1 : 1.99	0.55	0.60	0.30	0.35
17.72	26.50	1 : 1.54	2.20	2.20	1.40	1.45
23.97	23.48	1 : 1.01	9.40	9.60	8.05	8.35

[272] *Bur. of Standards Circ.* No. 62, 3rd ed., 22 (1923).
[273] Edeler, A., *Ind. Eng. Chem.*, **17**, No. 2, 196 (1925).

result shown in Tables 112 and 113. From this it appears that the more alkaline silicates give up a part of their soda content to neutral soap. It is well known to soapmakers that the silicious types of silicate are able to reduce the free alkalinity of an alkaline soap when the two are mixed in course of manufacture.

The determination of free alkali in a silicated soap by alcoholic extraction is thus a purely arbitrary procedure. The amount which appears will depend upon the ratio of the silicate present and will vary with the amount of water and silicate, i.e., upon the degree of hydrolysis. A more effective method as far as evaluation of the detergent is concerned could be worked out on the basis of the pH of the detergent solution at the concentration and temperature employed for the wash.[274-285]

TESTING DETERGENCY.

Practical Washing Tests. Analysis of a washing material may give useful information as to its origin and reveal some of its essential properties, but as yet the information thus gained must be construed with great caution and in the light of experience with actual washing operations.

Many workers have sought to establish simple tests by which detergency could be determined by measuring accurately one of the characteristics which affect the process of cleansing.[286] Such are the measuring of drop number, lathering power, and deflocculation, each of which is of use under a limited set of conditions.[287] Each fails to take fully into account the complicated nature of the washing process. Until the whole series of phenomena is more fully understood it seems logical

[274] *Proc. Am. Pharm. Ass.,* **42**, 608-609 (1894).
[275] *Chem. Zeit.,* **20**, pt. 1, 20-21 (1896); *J. Chem. Soc.,* **72**, pt. 2, 159-160 (1897).
[276] Hussein, Ahmed, *Pharm. J.,* **74**, ser. 4, **20**, 821 (1905).
[277] *J. Pharm. Chim.* (6) **21**, 496-497; *Chem. Zentr.,* **76**, II, 81 (1905).
[278] Braun, K., *Chem. Repertor.,* **31**, 355 (1907); *Z. angew. Chem.,* **21**, pt. 1, 1028-1029 (1908).
[279] Isnard, E., *Ann. Chim. anal.,* **19**, 98-100 (1914); *J. Soc. Chem. Ind.,* **33**, 362-363; *Chem. Ztg.,* **85**, I, 1522; *C. A.,* **8**, pt. 2, 2077 (1914).
[280] Leitch, Harold P., *Ind. Eng. Chem.,* **6**, 811-812 (1914).
[281] Deite, Carl, "Manual of Toilet Soap Making," trans. from Ger. by H. Keane. 2nd ed., London: Scott, Greenwood, **1920**, 326-327.
[282] Sheeley, M. B., *Chem. Bull.,* **8**, 275-276 (1921).
[283] Beedle, F. C., and T. R. Bolan, *J. Soc. Chem. Ind.,* **40**, 27-29T, 74T (1921); *C. A.,* **15**, 1925.
[284] *Ind. Eng. Chem.,* **14**, 1159-1163 (1922).
[285] Jones, H. E., *Brunner, Mond & Co. Booklet L-237.*
[286] McBain, J. W., R. S. Harbone, and A. M. King, *J. Soc. Chem. Ind.,* **42**, 373-87 (1923).
[287] Hillyer, H. W., *J. Chem. Soc.,* **25**, 511 (1903); Chapin, Robert M., *Ind. Eng. Chem.,* **17**, 461-465, 1187-1191 (1925); Spring, W., *Rec. Trans. Chim.,* **28**, 120-135, 424-438 (1909).

to resort to actual washing tests to evaluate detergents. But even this is beset with difficulties. Different fabrics do not behave alike when soiled with the same dirt. It is no simple matter to soil any kind of goods with perfect uniformity, so that concordant results can be had only with repeated tests of the same materials and even if this is accomplished it does not follow that the standardized experiment will faithfully represent the conditions of actual practice. Dirt is anything we wish to remove, and its chemical nature exceedingly miscellaneous.

Faragher [288] groups the materials encountered in industrial laundering into albuminous substances, such as blood and egg stains; vegetable dyes, which cause fruit and wine stains; fats and oils, including hydrocarbon greases and oils; acid and alkali stains; body excretions and waste epithelial cells; old starch; and street dirt and soot. So we shall have to apply reservations even here. A beginning has, however, been made.

Standard Soiling. Attempts to produce standard soils have been numerous, often based on convenience rather than on close analogy to working conditions. One of the best mixtures is that proposed by Shukoff and Schestakoff.[289] It is a mixture of lamp black with a solution of lanolin in benzene. The importance of uniform application of the soiling agent is stressed* Another mixture consists of linden charcoal, mineral oil, and fatty acid, while indigo colloid and a solution of machine oil in gasoline with and without starch have been employed.[290, 291]

Almost all the mixtures lay stress upon some form of finely divided carbon, doubtless partly because it is so easily seen. This may be misleading because other forms of dirt are quite as important in laundering, and it does not necessarily follow that a reagent which deflocculates carbon will react in the same way with clay or silica. For this reason the mixture of Shukoff and Schestakoff would more nearly simulate actual working conditions if clay or other silicious material were added. Starch generally makes washing easier by preventing the dirt from working into the fabric and by interposing a film which is easily wetted. Asphalt is not a normal soiling material and should not be used in a study intended for application to ordinary laundry practice.

There is a tendency to use a large amount of soiling material in test

[288] Rogers and Aubert, "Industrial Chemistry," Chapter XXVIII, by W. F. Faragher, New York: D. Van Nostrand & Co., 1912, 582-583.
[289] *Chem. Ztg.,* 35, 1027 (1911).
[290] *Z. deut. Öl-Fett-Ind.,* 41, 338-341.
[291] *Textilberichte,* 2, 37-38, 61-62 (1921).
* Note: A useful bibliography on the hydrolysis and detergency of soap solutions by L. W. Bosart was published in *Ind. Eng. Chem.,* 14, 1150 (1922).

washings, which is inadvisable, as detergent action depends in part upon the amounts of dirt and reagent.

Microscopical Examination.[292] A microscope is a very useful accessory to detergent testing. Two samples of cloth which look alike to the naked eye may show striking differences when thus examined.[293] Many of the effects of detergents are cumulative and become evident only after many cycles of washing, rinsing, and ironing. An occasional treatment with an abnormal amount of sodium carbonate seems to make little difference on white cotton goods, but if continued it yields a gray color by reflected light and, by transmitted light, a brownish tint.

Development of Standard Practice. The American Oil Chemists' Society has a committee on the evaluation of detergents which, in co-operation with various industries, is studying a test which by actual washing and measurement of color of standard fabrics having a standard soil will seek to put in the hands of investigators a set of conditions which will at least give results that can be duplicated. Until some such device is perfected we shall not be able to discriminate between different soaps for any one kind of washing or know accurately the place of silicate solutions in detergent operations short of the long process of trial and error conducted in practical operations over extended periods of time. This method, though it leaves much to be desired from a scientific viewpoint, yet yields authentic information to careful observers and it is thus that soluble silicates are accepted to-day on a large scale for both domestic and commercial washing.[294, 295]

[292] Detergent Com. reports in *J. Am. Oil Chem. Soc.*, **1925**, *et seq.*
[293] Stericker, Wm., unpublished report.
[294] Keit, *Deut. Washerei Ztg.; Seifensieder Ztg.*, **48**, 41-42 (1921); *C. A.*, **15**, 1413.
[295] Hoyt, L. F., et al., *Oil & Fat Ind.*, **3**, 156; D, 29-34 (1927); *C. A.*, **21**, 1198.

Chapter XI.

Gelatinous Films and Gels.

The coalescence and gelation of silica sols is determined by a set of conditions which have been only partly explored. Liesegang acidified a silicate solution with hydrochloric acid in excess. This stabilized the sol as a mobile liquid. When a piece of solid sodium hydroxide was dropped into the tube an alkaline layer was formed in which the sol was also fluid. Between the two, a thin film of gel progressed slowly upward in the tube. As the alkaline layer increased by diffusion it dispersed the gel, which continually formed anew at the point where neither acid nor alkali was in sufficient excess to prevent gelation, while both alkaline and acid sols in the same tube remained liquid. Gels may be formed in both acid and alkaline solutions by adjusting to concentrations of silica appropriate to the particular conditions, a variety of which will appear as we consider the industrial uses of silicious gels. Purity, time, and temperature play important rôles; but these influences affect the rate of coalescence rather than the fundamental tendency of sols to progress to larger and larger aggregation and finally to gel. After gelation the particles still tend toward rearrangement leading to syneresis and finally to crystal structure.[1]

The properties of the gel are changed by altering the amount of liquid present when it is formed. The number and size of the interspaces affect porosity, capillarity, and reaction rate of processes which occur at the surfaces. The presence of colloids other than silica may also affect the reactivity and usefulness of the gel.

For convenience in grouping the uses of silicious gels in industry, an arbitrary distinction is made between those gels which embody the entire reacting liquid and those which are formed as films.

Gelatinous Films.

Formation by Cataphoresis.

The passage of a direct electric current through a silicate solution causes cataphoresis. The positively charged sodium ions migrate toward

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[1] Scherrer, P., *Nachr. Ges. Wiss.*, **96**, 100 (Göttingen, **1918**).

the cathode and the negatively charged silica toward the anode. Unless the solution is agitated the concentration of silica at the anode surface soon reaches a point at which the sol is no longer stable, and a thin transparent film of gel is formed. This partially, but not completely, polarizes the cell and the current flows in much reduced amount, for the gel is a porous structure and contact can be maintained through it between the cathode and the main body of electrolyte. To the extent that current passes, however, the gel increases in thickness and finally the resistance increases to a point where there is practically no flow. Reversal of the poles will cause the gel to be dispersed unless the anode coating has become dehydrated, which may occur if there is enough current to cause a large local rise of temperature. The physical character of the film, like that of other gels, alters with concentration and any factor which affects the amount of silica present at the moment of gelation. So it is with all silica gels.

PREVENTION OF CORROSION.

Cleansing of Aluminum Ware. Metallic aluminum is rapidly attacked by hot solutions of sodium carbonate. Corrosion of aluminum wares cleansed with ordinary soda was measured by Seligman and Williams,[2] who found a loss of 5.3 grams per 100 sq.cm. in 24 hours at 75°C. with 5 per cent $Na_2CO_3 . 10H_2O$, and 80 grams were dissolved by a 1 per cent solution at 100°C. Pitting and discoloration may take place even at atmospheric temperature. High-ratio silicate solutions of the same sodium content do not attack aluminum. If a piece of aluminum is partly immersed in 1 per cent solution of $Na_2O, 3.3SiO_2$ and subsequently put into a 0.1 per cent solution of sodium hydroxide, bubbles of hydrogen appear at once on the untreated surface, but the silicate retards the action upon the treated part. NaOH solutions up to 0.5 gram per liter are practically without action on the silicate-protected surfaces. When a finger or even a soft rag is drawn across the treated surface it may be seen that the protection has been removed in the path traversed by finger or cloth. Close inspection will reveal the presence of a soft silicious gel upon the surface of the metal. In the first moments of contact between silicate solution and aluminum the metal begins to dissolve. Positively charged metallic ions are present at the exposed surface; they cause a concentration of negatively charged colloidal silica which was already tending to coalesce. The sol

[2] Seligman, Richard, and Percy Williams, *J. Inst. Metals,* **28,** 297-298 (1922) ; *C. A.,* **16,** 3803-4.

becomes unstable and separates as a protective film of gel upon the surface.

Small additions of silicates to carbonate solutions present the same phenomenon. The attack by a 5 per cent $Na_2CO_3 . 10H_2O$ solution is

FIG. 167.—Corrosion of 8 Cu—92 Al Sand Cast Porosity Cups. ZD Treatment vs. Norton Process vs. Heat Treatment Only *150 Hours* in 20 Per Cent Salt Spray.

ZD 8 Hr. Process (left). ZD 24 Hr. Process (left center). Norton 24 Hr. Process (right center). Heat Treatment Only (right).

arrested by one hundredth this amount of silicate of the more silicious kinds. Seligman and Williams found that 5 per cent $Na_2O, 2.2SiO_2$ did not attack the metal at 75°C.

Röhrig[3] extended the study to sodium sulfide solutions and found
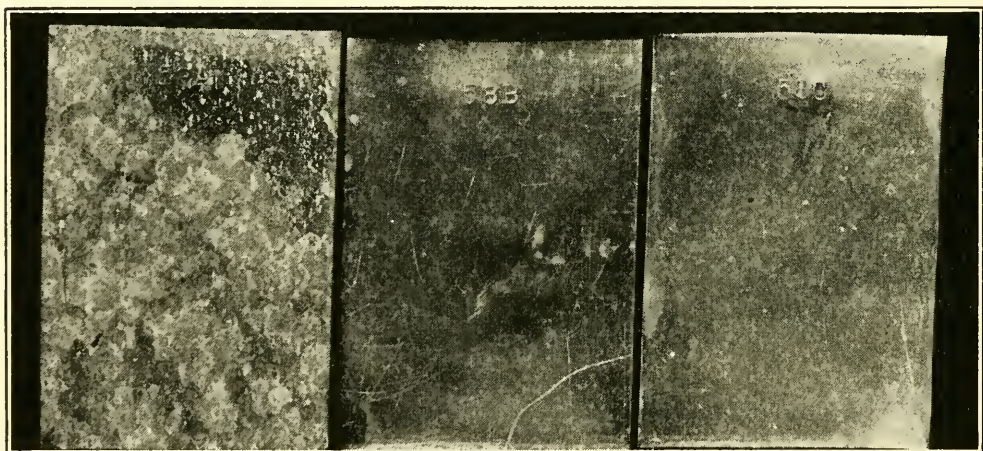
FIG. 168.—Soft-Annealed Sheet Aluminum—A. S. Spec. 11058 Exposed 120 Hours to Spray of 20 Per Cent Salt Solution.

No treatment (left). Treated Z-D Process (center). Twice Treated Z-D Process (right).

that similar films could be formed to protect aluminum containers for chemical reactions.

[3] *Chem. Ztg.,* **47,** 528-529 (1923) ; *C. A.,* **17,** 2983. For similar action on iron, see Rawling, Francis George, U. S. Pat. 1,566,118 (Dec. 15, 1925).

Zimmerman and Daniels [4] treat aluminum and alloys containing it by heating in silicate solutions and, after draining, baking the film at temperatures above the boiling point of water. A bright surface of metal may be preserved by immersing in $Na_2O, 3.3SiO_2$ 1.1 specific gravity for 2 hours at 65°C. (150°F.), removing the metal from the bath and baking for 20 hours at 148°C. (300°F.). A cast duralumin cup after treatment resisted a 20 per cent salt spray for 120 hours without signs of corrosion, though an untreated cup was corroded after 3 hours. A cup made from 90 per cent aluminum and 8 per cent copper when filled with a mixture of gasoline and water showed corrosion after 24 hours, but when treated it resisted corrosion for 135 days.[5]

Zinc Plates for Dry Battery. Zinc plates for dry battery cans can be made to corrode more evenly by treating them with a solution containing soluble silica. .Detergent action doubtless plays a part in this, but the thin film of gel which is deposited is also a factor in preventing localized action.[6]

Solution of Lead Retarded by Film. A series of observations by Thresh [7] points to film formation under conditions of extreme dilution. The plumbo-solvent moorland waters of certain districts in England have given frequent concern to the authorities on account of lead poisoning. Pure water does not dissolve lead, but water containing dissolved oxygen causes lead to go into solution, giving the water an alkaline reaction. The alkalinity of natural waters is not, however, a reliable index of their solvent power toward lead.

TABLE 114.

Substance Added	Value of pH	Appearance of Liquid after Acting on Lead	Oxygen Used, Per Cent	Amt. of Lead in Drawn-off Liquid Pts. per 100,000
Lime water	9	Turbid	90	9.35
Lime water and silicic acid....	9	Clear and bright	19	0.165
Lime water and citric acid....	9	Clear and bright	24	0.75
Sodium silicate and citric acid	4.5	Clear and bright	24	1.85
Citric acid only..............	4.5	Dull	76	2.05
Hydrochloric acid ($N/22$)....	4.5	Dull	80	7.0

Conductivity water was adjusted to pH 9 by adding lime water and dissolved 9.35 parts per million of lead. In the presence of colloidal

[4] U. S. Pat. 1,540,766 (June 9, 1925).
[5] Zimmerman, A. C., and Daniels, S., *Ind. Eng. Chem.*, 17, 359 (1925).
[6] Breyer, F. G., and W. H. Finkeldey, U. S. Pat. 1,451,758 (April 17, 1923) ; *C. A.*, 17, 1926.
[7] Thresh, John C., "Examination of Waters and Water Supplies," 3rd ed., Philadelphia: Blakiston, **1925**, 128-134.
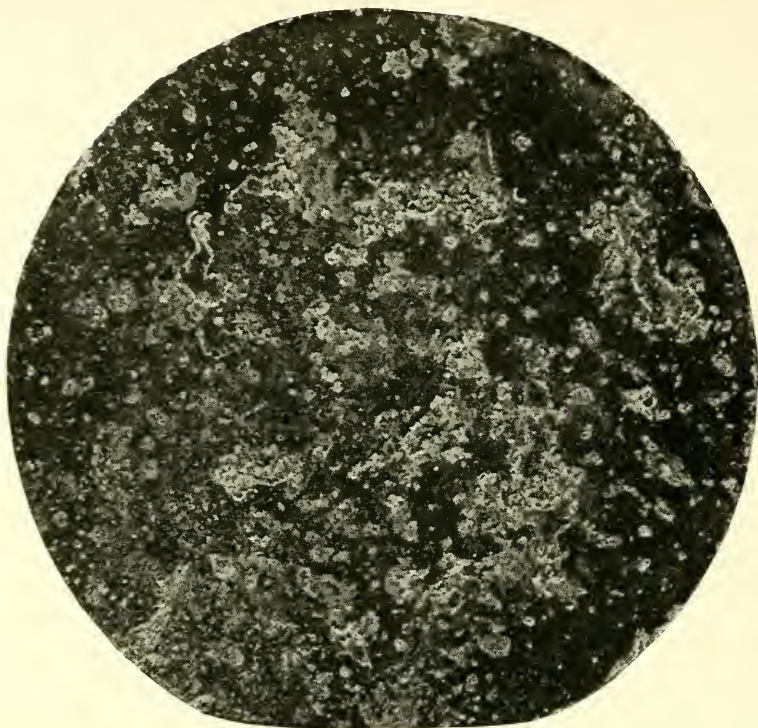
Fig. 169a.—Duralumin as Cast. No Silicate Treatment. Immersed 30 Days in Distilled Water.
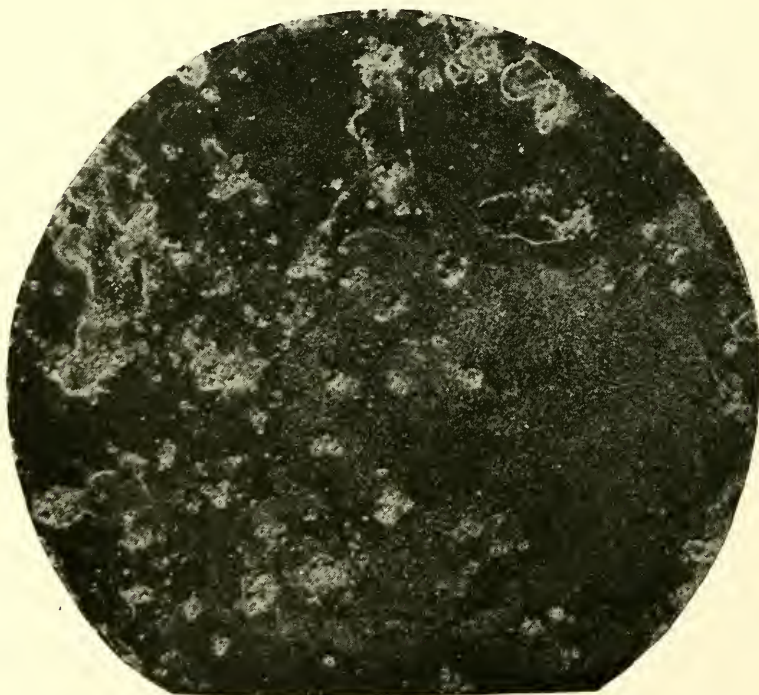
Fig. 169b.—Duralumin Heat Treated. No Silicate Treatment. Immersed 30 Days in Distilled Water.
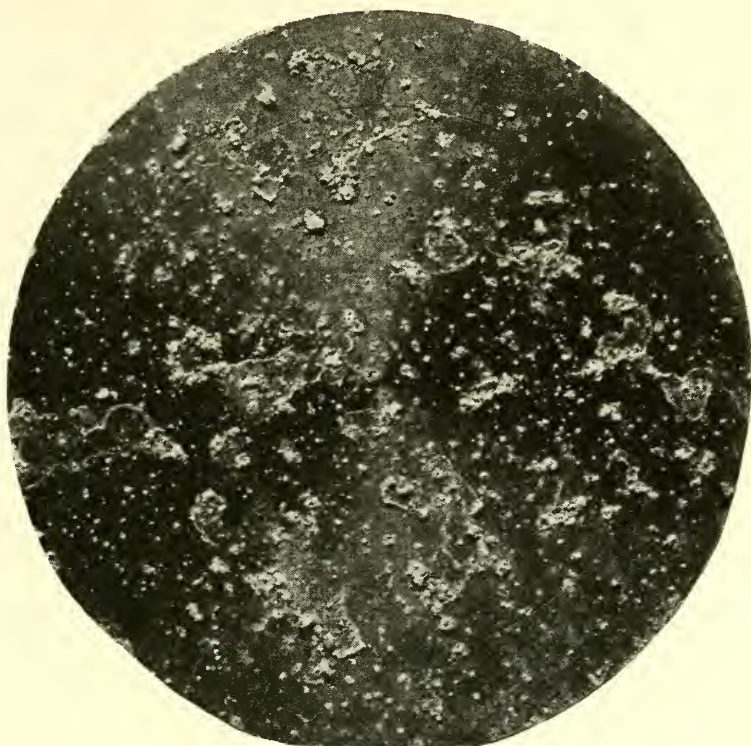
FIG. 169c.—Duralumin Machined. No Silicate Treatment.
Immersed 30 Days in Distilled Water.
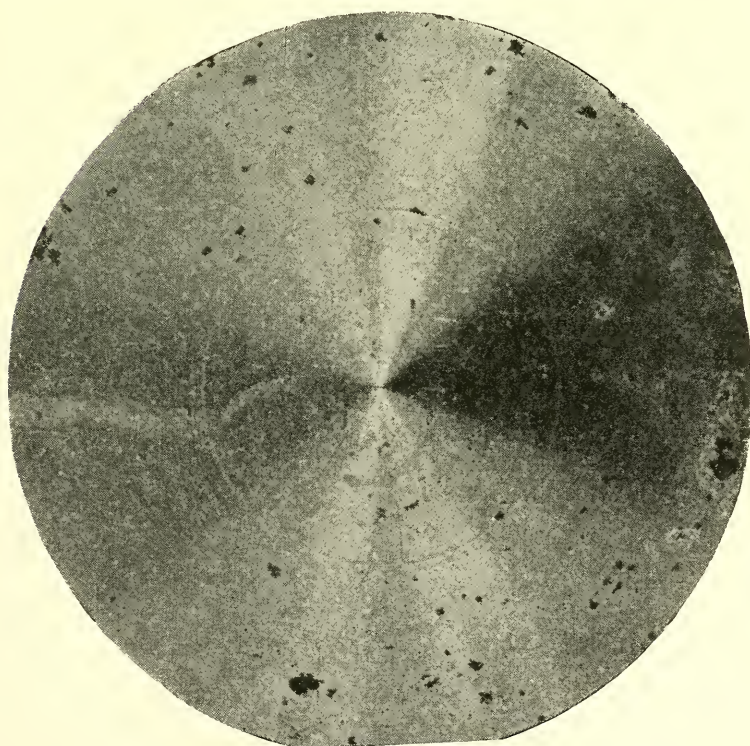
FIG. 169d.—Duralumin Machined. Treated by Z-D Process.
Immersed 30 Days in Distilled Water.

FIG. 170a.—Duralumin Machined. No Treatment. Exposed 120 Hours to Spray of 20 Per Cent Salt Solution.

FIG. 170b.—8% Cu—92% Al Machined. No Treatment. Exposed 120 Hours to Spray of 20 Per Cent Salt Solution.
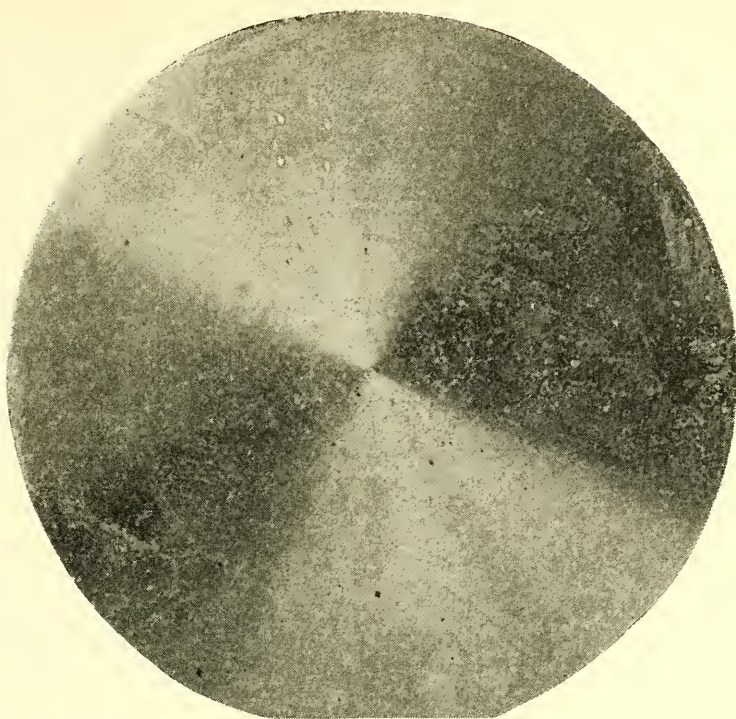
FIG. 170c.—Duralumin Machined. Treated by Z-D Process. Exposed 120 Hours to Spray of 20 Per Cent Salt Solution.

FIG. 170d.—8% Cu—92% Al Machined. Treated by Z-D Process. Exposed 120 Hours to Spray of 20 Per Cent Solution.

silica only 1.65 parts per million were dissolved. Although both col-loidal silica and soluble silicates retard the oxidation and solution of lead the latter are more effective. This is probably due to the texture of the film. Five parts per million of silica as soluble silicate are enough to reduce the solution of lead to a safe point in distilled water, but in the presence of carbonates or sulfates a much smaller quantity is sufficient.

TABLE 115. *Effect of 24-Hour Exposure on Solution of Lead.*

	Silicic Acid				Sodium Silicate as Silicic Acid			
In mgm. per 100cc.....	0.75	1.0	1.5	2.5	0.3	0.6	0.75	1.0
Oxygen used	0.95	0.94	0.95	0.37	0.87	0.325	0.130	0.15
=Lead oxidized	12.3	12.15	12.3	4.8	11.25	4.2	1.7	1.95
Appearance of liquid..	Sheeny	Turbid	Turbid	Clear	Dull	Clear	Clear	Clear
Lead in liquid	5.5	3.25	1.0	0.05	5.75	0.02	0.02	0.01

The amount of lead which can be tolerated is somewhat debatable but Thresh believes no harm can come from a water in which it never exceeds 0.5 part per million. The fact that the reaction is not completely suppressed suggests the formation of a gel film which is slightly permeable; but a film formed from a concentration of 5 parts per million would necessarily be tenuous; and a more even covering is to be expected from soluble silicate in which the degree of dispersion is greater than when silica, unprotected by sodium, is in a more advanced state of coalescence.[8]

Wet films of gelatinous silica as thin as these are not visible. They are not only very thin but translucent.

The following is a comparison showing the behavior of an English lake water before and after treating with silicate.

TABLE 116. *Effect of Silicate Treatment.*

	Untreated	Treated with Silicate of Soda
pH	6	7.5
Electrical conductivity	33	46
Oxygen removed in stagnant water in 24 hours, pts. per million....................	9.0 pts. per million	1.6
=Pb oxidized, pts. per million.............	115.6 " " "	20.7
Pb in solution, " " "	18.1 " " "	0.1
Pb in deposit, " " "	49.0 " " "	0.0
Pb on foil, " " "	48.5 " " "	20.6
SiO₂	Trace	8.5

Water from one of the most dangerous reservoirs at Glossop in Derbyshire was treated with silicate. Some days later a test of 17

[8] Thresh, John C., *Analyst*, **47**, 459-468, 500-505 (1922); *C. A.*, **17**, 3733.

houses showed 14 in which no lead could be detected; the others showed 0.3, 0.2, and 0.15 part per million. The untreated water would have contained near 0.9 part per million.

Prevention of Rusting of Iron. In the course of his work on the control of lead corrosion with silicates, Thresh observed, as Speller had done, that the rusting of iron was also inhibited. In Paignton, where the water is carried for 17 miles through iron mains, great annoyance had resulted from rusty water and frequent cleaning of the pipes was necessary to prevent complete stoppage. Sodium carbonate treatment did not improve the situation. When silicate was added some rust was deflocculated and thus removed, but in three days the water became clear and bright and continued in this condition. Ten parts per million of silica as silicates are usually sufficient to control the rust in a municipal supply. Change in the pH of water such as that
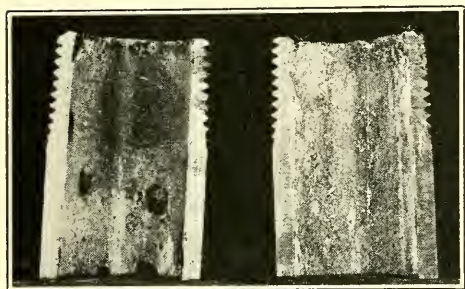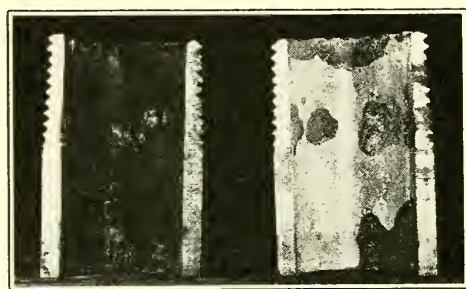
Black   Galvanized   Black   Galvanized

Fig. 171.—With Silicate Treatment.   Fig. 172.—Without Silicate Treatment.

induced by silicate treatment for corrosion may also serve to kill water-borne bacteria of the typhoid and cholera groups.[9]

Speller and his collaborators have worked upon the corrosion of iron in hot water. They found that this corrosion is a function of the dissolved oxygen content of the water and not primarily due to carbon dioxide as has often been assumed. It is not necessary to rehearse here the theory of corrosion except to say that dissolved oxygen can remove films of hydrogen which polarize cathodic areas of metal and when this occurs more iron passes into solution.[10, 11, 12]

The interposition of a silicious film prevents this transfer and stops

[9] Atkins, W. R. G., *J. State Med.*, **31**, 223 (1923); *App. Chem. Rept.*, **8**, 516.
[10] Speller, F. N., "Corrosion," reprinted from "Petroleum Development and Technology in 1926," Am. Inst. Min. Met. Eng., **1927**.
  Speller, F. N., "Corrosion, Causes and Prevention," New York: McGraw-Hill Book Co., **1926**.
[11] Whitman, W. G., E. L. Chappel, and J. K. Roberts, *Ind. Eng. Chem.*, **16**, 665 (1924).
[12] Bancroft, W. D., *J. Phys. Chem.*, **28**, 785 (1924).

corrosion. The effect is most easily seen by plotting the specific rate of corrosion based on oxygen absorption against time with and without the silicate treatment.

Here, as in the case of lead corrosion, the protective film does not
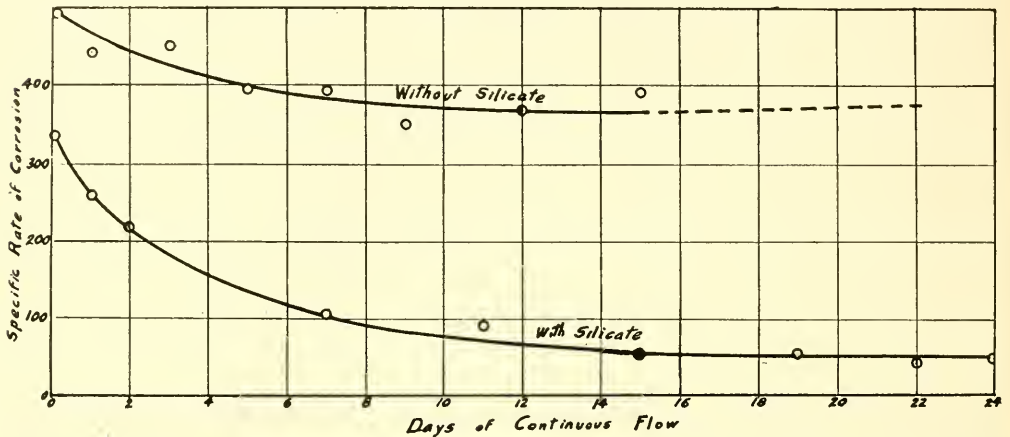
FIG. 173.—Corrosion Due to Water Flowing through Clean Black Steel Pipe at 43°C.

completely prevent the reactions which cause corrosion. Its permeable gel structure allows some reaction to occur. As a matter of experience, however, it has been found that that which continues after the film has formed is usually negligible.
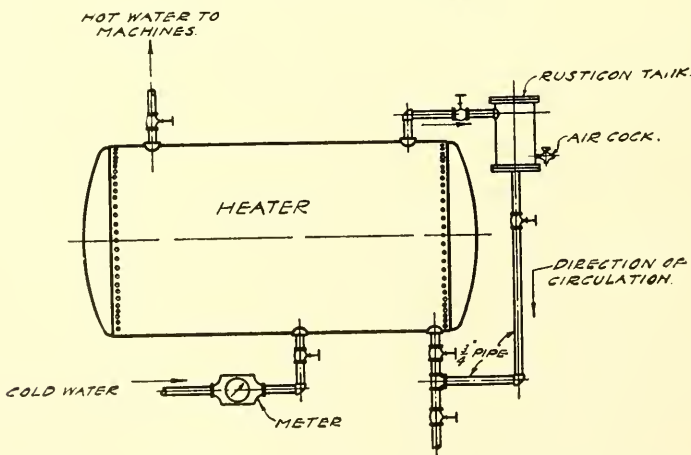
FIG. 174.—Application of Silicate to Prevent Rust in a Laundry Water Heater.

The technic of rust control of hot-water supplies with silicate solutions consists first in providing a concentration of about fifteen parts per million of $Na_2O, 3.3SiO_2$ to form the film, after which a dosage of five to ten parts per million suffices to maintain an adequate degree

of protection. Intermittent dosage may also be used but if the water is allowed to flow too long without silicate the film will be more or less dispersed and the protective effect will gradually decline.[13]

The deposition is greatest near the point where silicate is injected and it is best not to depend on protection in hot water through more than two hundred feet of pipe without a supplementary feeder. As previously indicated, cold water lines carry useful amounts of silica for miles. This conforms to the idea of gel formation, for colloidal silica proceeds to coalescence and gelation more rapidly at higher temperatures.

Gels are mechanically weakest when first formed, so weak in fact, that good films cannot be laid on surfaces where water is boiling actively or otherwise strongly agitated.

The hardening process or rearrangement of the gel particles by syneresis involves shrinkage which might expose portions of metal if no silica were present in solution to repair the defect. This and the tendency of the gel to disperse slowly are perhaps the principal reasons why the addition of SiO_2 to the water must be continued.

It was at first assumed that the film formation depended upon the formation of insoluble silicates, that is, upon heavy metal or alkaline earth metal salts in the water. Later it was found that good protection could be had in zeolite-softened water of zero hardness or even in distilled water. It is of course essential to apply the silicate in a way which enables the film to cover all the system, for otherwise corrosion would be concentrated in those parts not protected.[14-16]

Convenience dictates that a solid silicate be used for hot-water systems in homes and laundries as this requires a minimum of attention.[17] $Na_2O, 3.3SiO_2$ is best on account of its slow rate of solution. $Na_2O, 2SiO_2$ dissolves too fast at first and then tends to become incrusted by reaction with calcium and magnesium in the water. The advantage of a more even dosage is available for laundries and large installations by feeding a controlled amount of silicate solution into the water. This avoids not only variations in silicate concentration, but variations in ratio between Na_2O and SiO_2 inseparable from dissolving the solid on a small scale.

[13] Russell, Robert P., *Starch Room Laundry Jour.*, **94** (Dec. 15, 1923).
[14] *Chem. & Met. Eng.*, **31**, No. 15, 583-584 (1924).
[15] Texter, C. R., *J. Am. Water Wks. Assoc.*, **10**, 764-772 (1923); *Fire and Water Eng.*, **74**, 157-161 (1923); *J. Sanitary and Heating Eng.*, **102**, No. 10, 329 (1924); *Power*, **58**, No. 15, 588 (1923); *Nat. Assoc. Building Owners and Manuf.*, **117**, March 15, 1924.
[16] Speller, F. N., and C. R. Texter, *Ind Eng. Chem.*, **16**, 393-394 (1924).
[17] Speller, F. N., U. S. Pat. 1,531,992 (March 31, 1925).

Silicate may serve the double purpose of film former and binder for deoxidizing reagents in the form of briquets.[18, 19]

Analyses of scale from pipe systems in which corrosion has been stopped are not very satisfactory because of the difficulty of distinguishing between rust and the gel film. A further source of contamination lies in the calcium and magnesium compounds present in most natural water. Iron may be an essential part of the film, at least it is always evident in films from iron pipe. The small tendency of the film to build on itself may be due in part to the depletion of iron at the surface. The silicious film is in this respect very different from the calcareous protective films which stop rusting in very hard waters, and then build up serious obstructions to pipe lines.

Several partial analyses of silicious films, from Speller, are presented as typical.

TABLE 117. *Composition of Silicious Films from Silicate Treated Hot Water Systems.*

Location	Iron	Lime	Silica	
Chicago, Illinois	9.65	1.74	4.40	
Detroit, Michigan	16.05	1.78	5.30	
Pittsburgh, Pa.	53.75	5.75	2.93	(hot water tank)
" "	62.72	0.72	2.36	(1″ pipe from raw hot water)
" "	36.10	0.80	18.50	(after sodium silicate treatment)
" "	47.50	1.48	12.54	(¾″ pipe from hot water line 30′ from sodium silicate treatment tank)
Pittsburgh water	23.4	0.64	28.64	
" "	2.8	....	30.08	
" "	4.55	1.24	5.22	

Wherever the "red water plague" appears a judicious use of silicates will bring it to an end.

Silicate Films for Preventing Corrosion in Condenser Systems in Refrigerating Machinery. Silicate films for preventing corrosion have been successfully applied to condenser systems serving refrigerating machinery. Whitman, Chappell and Roberts [20] found that 0.250 kilo per m^3 (15.6 pounds per 1000 cubic feet, about 76 parts per million of SiO_2) of a 1.4 specific gravity solution of Na_2O, $3.3SiO_2$ reduced the corrosion rate in a recirculating system by 98 per cent and gave a high operating efficiency. Sodium dichromate also forms pro-

[18] Speller, F. W., U. S. Pat. 1,531,991 (March 31, 1925).
[19] Weidlein, E. R., "Strange Uses of Common Materials," *Management and Administration* (Dec., 1923).
[20] Whitman, W. G., E. L. Chappel, and J. K. Roberts, *Refrigerating Eng.*, **12**, 158-165.
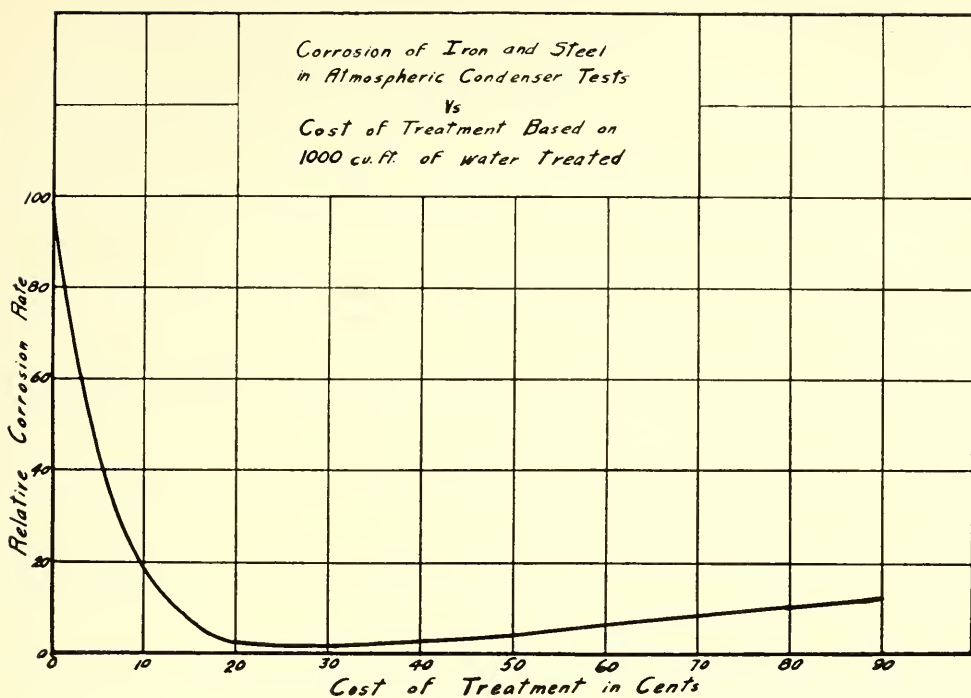
Fig. 175.
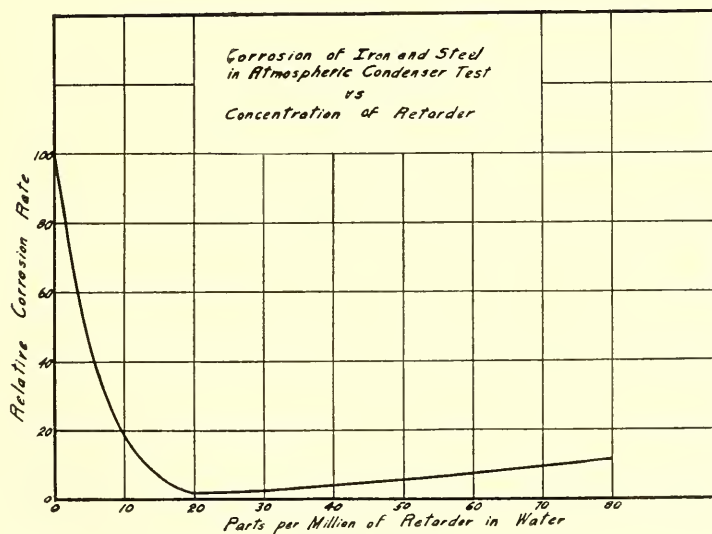
Fig. 176.

tective films,[21] but they are not permissible in potable waters nor do they endure in contact with pure water after the reagent is removed, as do the silicate films.

Use of Silicate Solutions in Sodium Chloride Brines. The use

[21] Russell, R. P., J. K. Roberts and E. L. Chappell, *Mass. Inst. of Tech., Serial No. 187*, **62**, No. 93 (1927).

of silicate solutions in sodium chloride brines is practiced in some plants.[22, 23]   It clarifies the brines and reduces corrosion; but silicates are not the ideal medium for this purpose because the brine hastens coalescence, and tends to cause an uneven film, with a tendency to pitting.   They have the advantage over chromates, however, that they do not cause the poisoning known as "chrome itch".

BOILER COMPOUNDS.

When soluble silicates are used as boiler compounds there always forms upon the inner surface of the boiler metal a thin silicious film, which is sometimes obscured by the use of extracts containing tannin which color the deposit so that it nearly matches the iron surface.   Such films have a use in reducing corrosion and appear to have no appreciable effect upon heat transfer.   They are very thin, highly hydrous, and, like the films used in the condenser systems, do not offer enough resistance to the conduction of heat to constitute an objection to their use.

A certain boiler operating in closed circuit with a high grade distilled water was treated with a silicate solution to control corrosion. Over a period of weeks in which no make-up water was added the concentration of silica and of sodium declined steadily, another bit of evidence of the deposition of a film.   Sodium is carried out of solution adsorbed on silica as it is in precipitation processes.[24]   Films formed under the conditions of boiler practice are never visible until the metal is dried, when they look like a thin covering of frost.   Many proprietary boiler compounds contain silicates of soda, the general function of which is to cause scale-forming material to precipitate in a flocculent condition in which it can be blown from the boiler, rather than as a crystalline, hard, adherent scale.   For example, see the patents of Schenitza [25] and Campbell.[26]

Silicious films formed in laundries and in textile establishments either for the purpose of preventing corrosion or incident to the use of the silicates as reagents for bleaching help to prevent the staining of goods by rust.   The silicates thus added also soften the water, save soap, and of themselves exert detergent action.[27, 28]

[22] Whitman, W. G., E. L. Chapell, and J. K. Roberts, *loc. cit.*
[23] Neff, J. W., *Ice and Refrigeration*, 6, 7, 383 (1924).
[24] Hecht, Max, personal communication.
[25] Schenitza, Philipp, U. S. Pat. 1,617,350 (Feb. 15, 1927).
[26] Campbell, James R., U. S. Pat. 1,278,435 (Sept. 10, 1918).
[27] Russell, R. P., *Starch Room Laundry J.*, Dec. 15, 1923.
[28] *Am. Ass. Textile Chem. Colorists*, 47-51 (1926); *Am. Dyestuff Rep.*, 15, 61-65; *C. A.*, 20, 896.

ELECTROLYTIC BATHS.

A variation of the application of silicious films to prevent corrosion consists in adding small amounts of silicate solutions to baths undergoing electrolysis. A thin film deposited upon the anode in the electrolytic reduction of nitrates or nitrites to ammonia practically eliminated the attack upon the iron anodes and greatly reduced the losses of nitrogen. A current density of five hundred amperes per square meter and an addition of 0.5 per cent of silica as silicate were employed.[29]

	With Silicate	Without Silicate
Bath tension	2.2 volts	3 volts
Losses of nitrogen..........	About 5%	As high as 60%
Utilization of current.......	About 90%	Below 50%
Corrosion of anode..........	Almost imperceptible	Several mm. per annum.

GALVANIZED IRON.

Galvanized iron is difficult to paint, but after treatment in a hot 1 per cent solution of silicate, which deposits a gel, it takes paint readily after drying. The gel presents a porous absorbent film which though very thin establishes a contact between metal and oil.

EGG PRESERVING.

Egg preserving seems little related to the process just cited, but consideration of the mechanism by which the respective results are secured shows them to be closely akin.

Technic. Of the many uses of silicate solutions, the practice of employing them for the preservation of eggs is, perhaps, the most familiar. Under the name of "waterglass," silicates of varying composition, concentration, and fitness for the work are sold and regularly used by great numbers of householders.

The process is essentially one of gelatinous film formation. The shell of the egg must be protected against the entrance of bacteria which cause decay. For this reason it is necessary to start with fresh, preferably sterile eggs. They should not be washed, as this removes a natural mucilaginous film and increases the danger of infection before the silicious gel has formed an effective seal. It is probable that both the albuminous constituents of the shell and the calcium compounds reduce the stability of the silica and thus aid the formation of gel. A silicate near the composition $Na_2O, 3.3SiO_2$ is best. It should be diluted just enough to allow the eggs to sink (about 4° Baumé) and put into a

[29] Grüner, V., U. S. Pat. 1,311,506 (July 29, 1919).

stone crock or other tight container. One U. S. gallon of specific gravity 1.38 will suffice for 50 to 80 dozen eggs, according to size of eggs and shape of container. The eggs are laid in the solution and kept covered by two inches of liquid till ready for use.

More dilute solutions can be used, but comparative tests indicate that when this is done the quality of the eggs after storage of six months or longer is inferior. Sometimes, especially if the container has not been tightly covered and the silicate has concentrated or absorbed much carbon dioxide, the whole of the liquid will gel. This does not affect the quality of the eggs; but because it is unpleasant to some people to put their hands into the soft gel to remove the eggs for use, a more stable silicate has been proposed. $Na_2O,2SiO_2$ under ordinary conditions of storage remains clear and liquid in contact with the eggs, but the preservation is not so good as that secured with the solutions containing more silica. This is manifest in an earlier thinning of the egg albumin and a depreciation of flavor due to the entrance, by dialysis, of trifling amounts of Na_2O.

FIG. 177.—Preserving Eggs in Silicate Solution.

High Quality of Eggs. Under optimum conditions, i.e., the right composition and concentration of silicate, storage in a temperature not above 25°C. and proper egg quality at the beginning of preservation, silicate storage gives eggs which are scarcely to be distinguished at the end of six months from fresh ones. It will always be observed that the shells have become harder and more brittle due to the silicious deposit in their pores. The sealing of these makes it necessary to prick a pinhole in one end of the egg before boiling, for otherwise the expansion of the ever-present bubble of air would cause the shell to burst.

Storage beyond a year is rarely desirable, though eggs will keep sweet in a silicate solution for at least two years. The membranes in the albumin weaken with time; but the thin whites are especially adapted for beating, as for making cakes, when they form a firmer mass of bubbles than do fresh whites. The uses to which stored eggs may properly be put are largely a matter of preference. Up to a year, they are quite wholesome and certainly adaptable to making cakes and custards, and to other cooking. Six months is perhaps as long as prime flavor can be expected in eggs served boiled or poached,

but this is equally true of other storage methods. When care is used to place sterile eggs in silicate within a few hours after laying, it is still possible after six months to break them into a dish and then carefully pick up the yolk by surrounding it with the thumb and four fingers and find the white sufficiently strong to be lifted also. This is a test used by poultrymen to characterize fresh eggs.

Dependence of Process on Gel Formation. Evidences that this process depends upon gel formation are the facts that other alkaline solutions have little value for preserving eggs, that dialysis of sodium oxide into the eggs will take place if the alkalinity of the solution is too high, and that eggs removed from the solution are protected for a longer time than fresh eggs, i.e., until the shrinkage of the gel permits the entrance of organisms able to cause decay. A bibliography of the literature of egg preserving with silicates is given below: [30-83]

[30] Nowotuy, E., *Poly. J.,* **143**, 238 (1857).
[31] Stead, Brit. Pat. 4,910 (1882).
[32] Ladd, E., *N. D. Exp. Sta., Bull.* (1897); also *U. S. Dept. Agri. Bull.,* **103**, (1897).
[33] Strauch, R., *Milchwirtschaft. Ztg.,* **26**, 342 (1897).
[34] Thieriot, J. H., *U. S. Consular Reports,* 563-564 (Dec. 1897).
[35] Jarvis, L. G., *Ontario Agri. College and Exp. Farm Report,* 193-196 (1898).
[36] Ladd, E., *N. D. Expt. Stat. Bull.,* **35**, 330-332 (1898).
[37] Jarvis, L. G., *Ontario Agric. College and Exp. Farm Report,* 130-134 (1899).
[38] *Queensland Agric. J.,* **4**, 418-419 (1899).
[39] Schutt, F. T., *Canada Expt. Farms Report* 223 (1899).
[40] *U. S. Agric. Dept. Bull., Farmer's Bull.,* No. 103, 32 (1899).
[41] Gilbert, A. G., *Canada Expt. Farms Report,* 251-277 (1900).
[42] Borntraeger, H., *Oesterr. Chem. Ztg.,* **3**, 295 (1900).
[43] Graham, W. R., *Ontario Agri. & Exp. Union, Report,* 31-3 (1901).
[44] Brigham, A. A., *Rhode Island State Exp. Stat., Report* 304, 6 (1901).
[45] Rylander, J. A., Brit. Pat. 23,523 (1901); *J. Soc. Chem. Ind.,* **21**, 183. See also U. S. Pat. 696,495 (1902).
[46] Brown, E., *J. Board Agric.* (*London*), **9**, 494-497 (1903).
[47] Guenther, Richard, *U. S. Statistics Bureau, Dept. of Commerce & Labor, Consular Reports,* No. 276, **73**, 66-67 (1903).
[48] Irwell, L., *Dietet. and Hyg. Gaz.,* **20**, 1096 (1904).
[49] Jeffrey, J. S., *N. C. Exp. Stat. Bull.,* **191**, 11-17 (1905).
[50] Langworthy, C. F., *U. S. Dep. of Agric., Farmers' Bull.,* No. 128, 34-35 (1906).
[51] Thatcher, R. W., *Wash. Stat. Bull.,* **71**, 14 (1907).
[52] Prall, F., *Z. Nahr. Genussm.,* **14**, 445 (1907).
[53] Bell, G. Arthur, *U. S. Dept. of Agric., Farmers' Bull.,* No. 287, 41-42 (1907).
[54] Hendrick, J., *J. Agric. Soc.,* **2**, 100 (1907); *Chem. Soc. Rept.,* **3**, 292.
[55] Vosseler, J., *Der Planzer,* **4**, 129 (1908); *Chem. Zentr.,* **19**, 11, 1214.
[56] *Pennsylvania Agric. Exper. Stat., State College, Bull.* **87**, 48 (1908).
[57] Lamson, G. H., Jr., *Conn. Storrs Agric. Exper. Stat. Bull.* **55**, 203-214 (1909).
[58] *Arizona Agric. Exp. Station, Tucson, Bull,* **60**, 398-464 (1909).
[59] Berger, Richard, *Z. Chem. Ind. Kolloide,* **6**, 172-174 (1910).
[60] Delaroquette, M., *L'ind. beurre,* **1**, 600-603 (1910).
[61] Berger, R., *J. Ind. Eng. Chem.,* **3**, 493-495 (1911).
[62] Lamson, G. H., *Conn. Agric. Exper. Stat. Bull.,* **67**, 269-274 (1911); abs. in *Chem. Zentr.,* **82**, 11, 780.

Gels.

Conditions Necessary for Formation.

The diversity of conditions under which silica forms protective films invites the question of what the general conditions are under which we may expect their deposition to take place. The films are like gels which include the whole mass of reacting liquids except that they are laid down from systems which contain much more water and result from a condition at a surface. This may render colloidal silica unstable by chemical reaction or its concentration may be increased locally by electrical forces.

The conditions of gel formation are those which make colloidal silica unstable or permit the process of coalescence to proceed. The rate at which this occurs is greater in concentrated than in dilute solutions. It is accelerated by heat and retarded by cold. Like charges upon the colloidal particles increase their repulsion of each other and help keep them dispersed. Thus either strongly acid or strongly alkaline solutions are more stable than those near neutrality. Acids have less effect than alkalies, which, as we have seen, are able permanently to stabilize the solutions.

Numerous data on the conditions of gel formation were obtained by Flemming.[84] He was not able to check the statements in the older

[63] Vanderleck, J., *American Food J.,* **6,** No. 11, 13-14 (1911).

[64] Bartlett, J. M., *Maine Agric. Exp. Station, 8th Inter. Cong. Appl. Chem.,* **18,** 51-56 (1912).

[65] Benjamin, Earl W., *Cornell Reading Courses for the Farm Home,* **1,** 300 (1912).

[66] Evéquoz, A., and E. P. Häussler, *Zeit. Nahr.-Genuss.,* **25,** 96-97 (1913).

[67] Flohr, Lewis B., *U. S. Dept. of Agric., Farmers' Bull.* **594,** 4 (1914).

[68] *Arizona Agri. Experiment Station Record,* **32,** 870 (1915).

[69] Wing, Annie L., *J. Home Econ.,* **7,** 257 (1915).

[70] Arnoux, André, *Compt. rend.,* **163,** 721-722 (1916).

[71] Alder, Byron, *Utah Agric. Exper. Stat., Logan, Circ.* **25,** 6 (1917).

[72] Heiduschka, A., *Chem. Zentr.,* **88,** ser. 5, 21, pt. 2A, 116-117 (1917).

[73] Slocum, Rob R., *U. S. Dept. of Agric., Farmers' Bull.* **889,** 21-22 (1917).

[74] *Chem. Ztg.,* **41,** 440, 477, 691-692, 848.

[75] Reinthaler, *Chem. Ztg.,* **42,** 195 (1918).

[76] Dvorachek, H. E., and S. R. Stout, *Expt. Stat. Record,* **39,** 781 (1918).

[77] Hasterlik, Alfred, *Zeit. Nahr.-Genuss.,* **48,** n.s., **36,** 170 (1918) ; *Pharm. Zentr.,* **58,** 265-266.

[78] Olson, G. A., *Wash. (State) Agric. Expt. Stat., Popular Bull.* **114,** 1-3 (1918).

[79] Love, Fanny, *National Stockman and Farmer,* **43** (1919).

[80] *U. S. Dept. of Agric., Weekly News Letter,* **6,** No. 46, 9 (1919).

[81] Jones, H. I., and R. Dubois, *J. Ind. Eng. Chem.,* **12,** 751-7 (1920).

[82] *U. S. Dept. of Agric., Dept. Circ.* No. 15, 3 (Boys' and Girls' Poultry Club Work).

[83] Dunbar, Ruth, *Country Gentleman,* **85,** pt. 2, 46-47 (July 31, 1920).

[84] Flemming, W., *Z. Phys. Chem.,* **41,** 427-457 (1902).

literature that stirring or the presence of graphite, taken as typical of foreign solids, affected the time of setting. His work leaves much to be desired because it charts a very limited set of conditions, but it was carefully carried out and can best be presented by a series of tables and graphs. He found that differences in the purity of silicate solutions such as those between commercial products and specially purified preparations were unimportant as far as time of gel formation was concerned. Hydrochloric acid causes a slightly faster gelation than sulfuric acid though on the basis of normality the times are similar. A comparatively narrow range of concentrations was covered and no consideration was given to the many other compounds which can be used to cause silica to gel. The presence of other electrolytes in the silicate, as well as the manner of mixing, is known to have a great effect on time and on physical character of the resultant gel. Flemming made all his gels by pouring silicate into acid, as he could in this way prevent immediate precipitation in many cases by providing for a local excess of acid in the mixing process.

The process of coalescence may be interrupted, as by adding fresh silicate solution to one that has been neutralized but has not yet gelled. Such a solution when used as a vehicle for pigments and spread out as a paint becomes unstable on drying and is less soluble than a straight silicate film.

Carter found that Na_2O, $3.3SiO_2$, 1.38 specific gravity, can be made to form a uniform gel by stirring in hydrochloric acid diluted to 1.009 (5 volumes concentrated hydrochloric acid to 100 volumes), and concentrated hydrochloric acid (39.11 per cent, 1.20 specific gravity) may be stirred into the silicate solution at a concentration of 1.03 specific gravity (4.5°Baumé) (1 part of silicate by weight to 10 parts of water by weight), in either case without instant precipitation. Of course vigorous stirring is necessary.[85]

Concentration. If the ratio of silica to water in a silicate solution is one to 300 mols or less, the whole solution, when partly or completely neutralized, may set to a solid gel.[86] One mol of silica makes with 300 mols of water a gel which is soft and weak, and which soon squeezes out some of the liquid phase by syneresis, or upon stirring becomes a gelatinous precipitate at the bottom of its container with a relatively large volume of supernatant liquid. As the ratio of water to silica in the reacting liquids declines, firmer and firmer gels

[85] Unpublished data of the Philadelphia Quartz Company.
[86] Holmes, H. N., *Colloid Symposium Monograph*, **1**, 25 (1923).

are formed, first stiff friable jellies and finally hard strong grains having the superficial appearance of sand. The so-called silicate cements used in dentistry are strong and durable. They depend upon the formation of a gel from hydrous silica dispersed with phosphoric acid in the presence of small amounts of water.[87, 88] The acid-resisting cements described in Chapter VII, made from silicate solution dried with inert filler and then treated with acid, also contain a hard gel formed in the presence of about 20 per cent of water which is quite
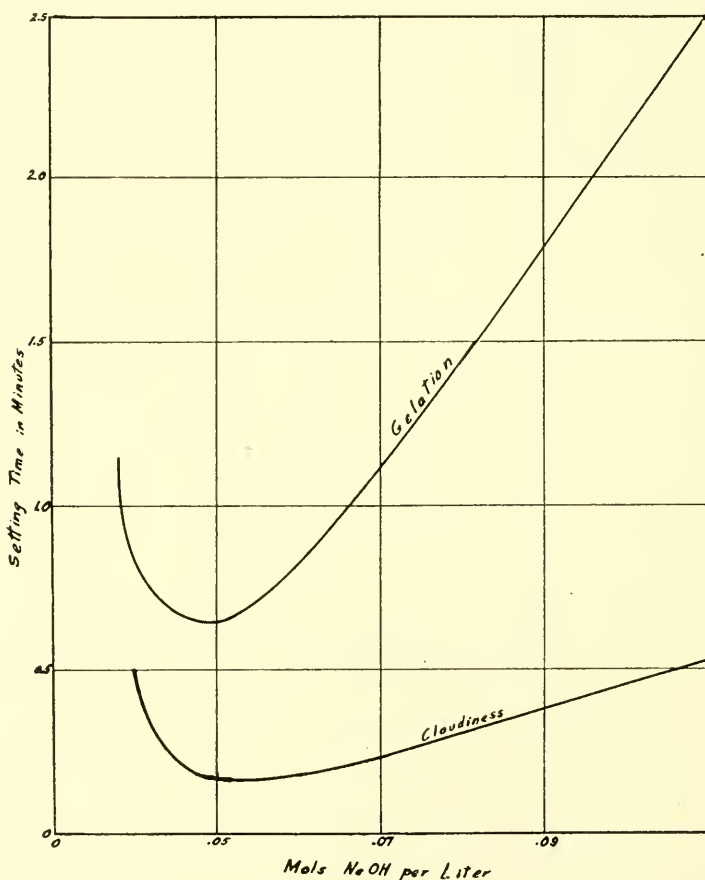
Fig. 178.—Turbidity and Gelation (Flemming).

different in texture from gels which form in the presence of much water. The amount of water in the system at the time of setting determines the structural arrangement of the solid phase and such gels are therefore different from those from which the water is removed

[87] Weiser, Harry Boyer, "The Hydrous Oxides," 1st ed., New York: McGraw-Hill Book Co., **1926**, 175 *et seq.*
[88] Crowell, Walter S., Am. Inst. Chem. Eng., Cleveland Meeting, May 31 to June 3, 1927.
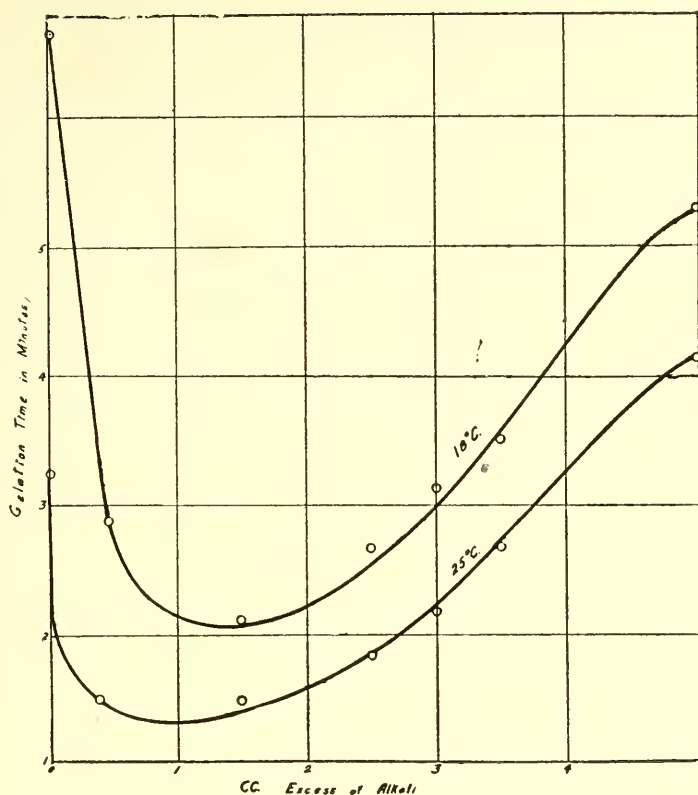
FIG. 179.—Effect of Alkali on Setting Time (Flemming).
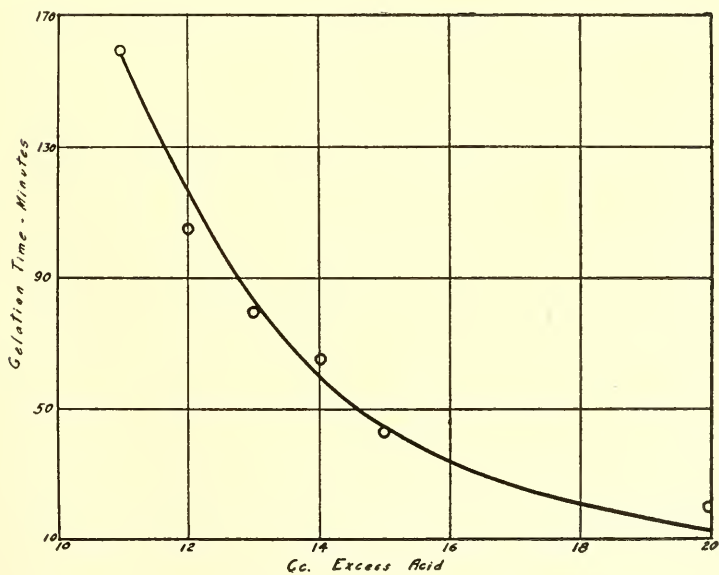
FIG. 180.—Effect of Acid on Setting Time (Flemming).

after they have assumed the solid form.   Concentration is therefore a vital factor in determining the properties of a silicious gel.

Temperature.   Temperature is also important for it affects the rate of coalescence, and if we think of the gels as structures built up by the aggregation of colloidal particles we should expect the most orderly and the strongest arrangement to occur where the transition was gradual.   This is confirmed by experience.   If conditions are so chosen that reaction is immediate no homogeneous gels can be had, but if the reaction rate can be reduced, as by cooling, the same solutions may yield a uniform translucent gel including the whole mass of the mixed solutions.

Acidity and Alkalinity.   Gels can be made in both acid and alkaline solutions although both acid and alkali tend eventually to stabilize the silica and make the gel form more slowly.

Flemming [89] noted the appearance of turbidity on a curve substantially parallel to that which marks the passing from liquid to solid.   A sharp rise of viscosity takes place very shortly previous to the actual setting.

TABLE 118.   *Effect of Alkali and Acid on Gelation.*

125cc. total volume
25cc. standard HCl (1.83 N.)
25cc. standard silicate containing 8.969% SiO_2
Sol. contains 1.795% SiO_2

Excess Alkali,*	Gelation Time, Minutes	
cc.	18°C.	25°C.
0.0	6.75	3.17
0.5	2.90	1.50
1.0	2.10	1.33
1.5	2.12	1.45
2.	2.22	1.67
2.5	2.67	1.83
3.	3.13	2.17
3.5	3.50	2.67
4.	4.08	3.17
5.	5.22	4.08

Excess Acid,		
cc.		
11	160	
12	105	
13	80	
14	65	
15	43	
20	20	

* Excess alkali added as NaOH.

[89] *Z. Phys. Chem.,* **41**, 427-457 (1902).

TABLE 119. *Time of Gelation.*
(Flemming)

Alkaline Sols

Mols SiO₂ per Liter	Time to Gel Minutes
0.270	0.81
0.2–22	2.92
0.135	34.45

Acid Sols

0.663	21.12
0.707	15.15
0.757	10.00

TABLE 120. *Effect of Temperature.*

Alkaline Sols

Temperature °C.	Time to Gel Minutes
35	14.05
45	8.65
55	4.82

Acid Sols

25	10.00
30	7.25
35	5.15
40	4.12

TABLE 121. *Setting Time Related to Content of Acid and Alkali.*
(Flemming)

Constant

Total volume	40cc.
Silicate volume	10cc.
N HCl volume	10cc.
Silicate contains 2.3 mols. SiO₂	
Mixture contains 0.575 " SiO₂ + xNaOH or HCl	
$\times$ 60	

34.500 gm. per liter

Mols NaOH per Liter	Mols HCl per Liter	Average Setting Time in Minutes
0.225	....	26.00
0.150	....	10.25
0.118	....	3.25
0.085	....	2.75
0.050	....	2.25
0.025	....	1.00
0.005	....	5.00
0.000	0.000	2300.00
....	0.015	7040.00
....	0.025	24540.00
....	0.075	29400.00
....	0.138	26640.00
....	0.325	16560.00
....	0.890	3580.00
....	1.830	1200.00

TABLE 122.

1.625 per cent SiO_2

Mols NaOH per Liter	Setting Time Minutes
0.0284	1.33
0.0341	0.82
0.0398	0.83
0.0455	0.89
0.0569	0.95
0.0798	1.43
0.1139	2.40

4.57 per cent SiO_2

Mols HCl per Liter	Setting Time Minutes
4.07	23.6
4.28	17.08
4.49	14.33
4.71	12.17
4.92	11.57
5.13	10.00

Vinal [90] investigated the proportions of strong sulfuric acid and silicate solutions needed to form solid electrolytes in storage batteries.

Time of setting before solidification takes place, and the stiffness of the jelly afterwards, are regulated by the proportions of the acid and silicate. When thickening of the mixture begins, the final setting process occurs within a very few minutes. An interesting time reaction is represented by this mixture, if it is made from dilute solutions, as for example, H_2SO_4 specific gravity 1.275 and silicate of specific gravity 1.210; the greater the percentage of silicate in proportion to the acid, the more quickly the jelly sets and the more solid it becomes. The hard jellies are resonant.[91, 92]

Different acids give similar results on the basis of normality. Hydrochloric acid is somewhat faster than sulfuric.[93, 94]

Jelly electrolytes may be made from mixtures of concentrated sulfuric acid and dilute solutions of silicate or from dilute solutions of the acid and somewhat more concentrated solutions of the silicate. Vinal shows that the time of setting is shortened by increasing the percentage of silicate and by using stronger acid. It is possible to prepare the jelly as a clear, translucent, bluish mass which varies in consistency

[90] Vinal, George Wood, "Storage Batteries." New York: John Wiley & Sons, **1924**, 121 et seq.

[91] Williams, Albert H., U. S. Pat. 1,403,462 (Jan. 10, 1922).

[92] Thatcher, Charles J., U. S. Pat. 1,393,467 (Oct. 11, 1921), covers another application in storage batteries.

[93] Electro-Osmose Ges., Aus. Pat. 102,961.

[94] Poulsen, A., Brit. Pat. 491 (1909); U. S. Pat. 1,012,911; Fr. Pat. 410,716.

from a thick liquid to a fairly hard resonant solid. The time of setting for various combinations is shown in Figure 181. The curves are numbered from 1 to 11 and represent different proportions of the silicate and acid solutions measured by volume, as follows:

Curve 1, 5 parts 1.275 acid to 1 part silicate
"   2, 4 parts 1.275 acid to 1 part silicate
"   3, 3 parts 1.275 acid to 1 part silicate
"   4, 2 parts 1.275 acid to 1 part silicate
"   5, 5 parts 1.400 acid to 1 part silicate
"   6, 4 parts 1.400 acid to 1 part silicate
"   7, 3 parts 1.400 acid to 1 part silicate
"   8, 2 parts 1.400 acid to 1 part silicate
"   9, 1 part 1.840 acid to 4 parts silicate
"   10, 1 part 1.840 acid to 3 parts silicate
"   11, 1 part 1.840 acid to 2 parts silicate

Use in Storage Batteries. According to Vinal, batteries containing jelly electrolytes do not have as good electrical properties as those
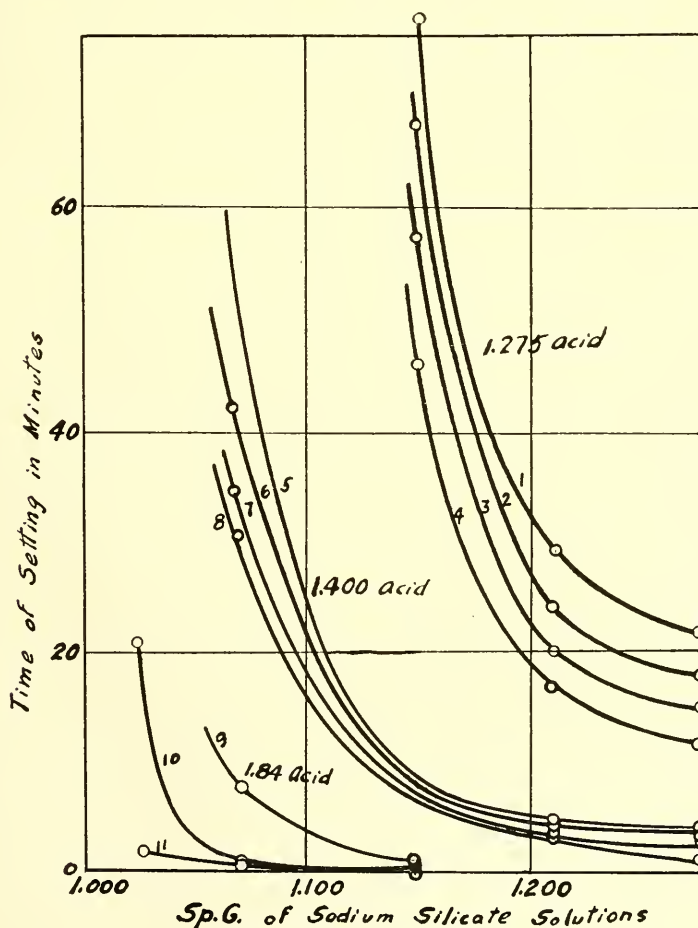
Fig. 181.—*Preparation of Jelly Electrolytes from Sulfuric Acid and Silicate of Soda.*

with the ordinary electrolytes. The internal resistance is higher and the capacity lower. They do not last well in service.

Since the jelly formed by the action of the silicate and the acid has a tendency to crack away from the plates of the storage battery, owing to shrinkage occurring because of the evaporation of water, Schoop has advocated the addition of paper stock, cellulose, or asbestos to the mixture to serve as a binder. In preparing this material for use, the silicate is poured into the acid and thoroughly mixed. The binding material is then added, and the mixture allowed to stand until thickening of the solutions is observable. When this point comes, it is necessary to pour the electrolyte into the cells immediately, as it is impossible to do so after solidification has actually taken place. When the electrolyte is prepared in this manner, it will not stick to the plates. Gas bubbles, which are formed at the plates during the process of the charging, will have an opportunity to escape between the plate and the solid electrolyte. A layer of fluid electrolyte is desirable between the solid electrolyte and surface of the plate. This facilitates the reactions within the storage battery and increases the capacity. Schoop [95] obtained a patent on jelly electrolytes in 1889. His experiments were further described in 1890.

Resistance of a solid electrolyte of this character is approximately double that of the ordinary liquid electrolyte. Local action is considerably increased and the capacity of the cells reduced. The use of such electrolytes may be found desirable for special work, not for ordinary types of service. The use of sodium silicate for the preparation of solid electrolytes has been periodically rediscovered a number of times during recent years.[96-99] Its use, however, dates back probably thirty years.[100] A clear detailed description is given by Schoop.

Batteries filled with hard grains of silica gels, which have been formed separately, dried, and washed, do not splash, and have better electrical properties than do those with gels formed *in situ*.

Gels Formed by the Action of Salts of Heavy Metals. Gels have also been made by reaction between silicate solutions and salts of various metals. Organic compounds, such as phenols and aldehydes, which

[95] *Electrotech. Z.,* 10, 473 (1889) ; *Electrician,* 25, 253 (1890).
[96] Winkler, C. F., U. S. Pat. 471,590 (March 29, 1892).
[97] Hirsch, H. H., U. S. Pat. 1,183,009 (May 16, 1916).
[98] Williams, H. M., U. S. Pat. 1,417,007 (May 23, 1922).
[99] Hacking, E., U. S. Pat. 1,421,217 (June 27, 1922).
[100] "Das Sekundar Element," *Encyklopädie der Electrochemie,* IV, Part 2, 140 (1895).

can react with sodium may also release silica to form gels.[101-103] Alkaline aluminates are also useful [104-106]—thus gels may be formed which contain colloids other than silica and which combine with the structural properties of the gel a specific chemical value which comes from the added material. Gels may thus be used as media of great surface to carry catalysts. Base exchange reactions used in softening water are also rendered more efficient by taking advantage of gel surfaces.[107-109]

To prepare gels for technical use, washing to remove reaction products is usually the next step. In the case of ordinary silica gel, water alone is required, but the process is a slow one, as time is required to allow diffusion through the pore structure to take place. Holmes varies the porosity of the final product by using a salt of iron, nickel or other heavy metal as reagent to cause gelation and then dissolving it out with acid, thus leaving in addition to the natural porosity the space occupied by the metal.

DRYING AND REHYDRATION.

Van Bemmelen's Results. Drying and rehydration of silica gels has been studied by Van Bemmelen.[110] Shrinkage occurs with drying down to about two mols of water. Near this point the clear gel begins to show cloudiness and gradually becomes opaque only to become clear again in the region of one mol of water. Though these points are quite definite for a particular sample of gel, samples vary greatly according to the manner of their preparation and it must not be assumed that definite hydrates are involved. The range for the first point is about 1.5 to 3 and for the second 0.5 to 1.

Molecular Rearrangements. The rearrangement of particles which results in gel formation does not cease at that point but continues with syneresis and drying shrinkage. Old samples of silica gel exhibit crystalline structure as shown by the diffraction of X-rays and this may be looked upon as the result of continued action of the same forces

[101] Marcus, R., Ger. Pat. 279,075 (1914).
[102] Michael, J. and Co., Ger. Pat. 348,769 (1922).
[103] Van Baerle, A., Swiss Pat. 93,268.
[104] Holmes, Harry N., and J. A. Anderson, *Ind. Eng. Chem.*, **17**, 280 (1925).
[105] Behrman, Abraham S., U. S. Pats. 1,515,007 (Oct. 8, 1927); 1,584,716 (May 18, 1926); Brit. Pat. 277,082 (Nov. 2, 1927).
[106] Wheaton, H. J., U. S. Pat. 1,586,764 (June 1, 1926).
[107] Patrick, Walter A., U. S. Pat. 1,577,186 (March 16, 1926); U. S. Pat. 1,577,190 (March 16, 1926).
[108] Chemische Fabrik auf Aktien Vorm. E. Schering and W. Klaphake, Brit. Pat. 250,078 (July 20, 1925); *C. A.*, **21**, 995.
[109] Govers, Francis X., U. S. Pat. 1,504,549 (Aug. 12, 1924).
[110] *Z. anorg. Chem.*, **13**, 233 (1896).

which cause gelation.[111]   Morey [112] has found that the treatment with
steam at 4-5 atmospheres of a certain alumino-silicate gel which does
not show crystal structure when dried below 100°Centigrade, causes
a rearrangement of the particles in such a way that an X-ray diffrac-
tion pattern is obtained.

Porosity of Silica Gel.   The thermal history of silica gel makes
great differences in its physical character.   Holmes [113] proposes moist
heat treatment to increase porosity by inducing set before the shrinkage
of the usual drying process has reached its limit.   In this way he was
able to make gels with an increased capacity for the condensation of
vapors.   The method is proposed as a general means of producing gels
of the right porosity for any given use.

The size of capillaries best adapted for the condensation of one liquid
is not necessarily best for another.   Also the conditions which deter-
mine the properties of the gel are difficult to reproduce and different
experimenters may easily obtain discordant results.   The exact control
of such factors—concentration, acidity or alkalinity, heat treatment and
rate of drying—is a necessary basis of technical preparation of sili-
cious gels.

Absorption of Moisture.   Dry silica gels absorb moisture with
great avidity.   They are much more efficient than calcium chloride for
drying air for laboratory purposes.   Two major industrial uses based
on this property have been proposed.   Plant designs have been drawn
for drying air for blowing blast furnaces by exposing it to finely di-
vided silica gel which is continuously removed from the system and
re-activated by heat.   The removal of moisture can be made quantita-
tive and the advantages of dry air are great.[114]   The problem is one
of cost.

Heat absorption by evaporation of water or other volatile liquid into
an atmosphere the vapor pressure of which is reduced by condensation
of the evaporating liquid in the pores of silica gel is used to produce
artificial refrigeration.   The gel requires only a source of heat to drive
off the absorbed liquid and the cycle may be repeated indefinitely.[115]

Condensation due to the lowering of vapor pressure in a small open-
ing does not alone account for the accumulation of vapors in silicious
gels.   Surface phenomena also come into play and water is specifically
adsorbed on these surfaces, as may be shown by a study of volume

[111] Scherrer, P., *Nachr. Ges. Wiss.*, Göttingen, **96**, 100 (1918).
[112] Morey, George W., personal communication.
[113] Holmes, Harry N., *Ind. Eng. Chem.*, **18**, 386 (1926).
[114] Silica Gel Corporation, Baltimore, Md., Bulletin No. 2 (1921).
[115] Fulton, *Chem. Age,* **31**, 521 (1923).

changes of supercooled systems. The adsorbed moisture does not freeze or increase in volume with falling temperature.[116]

ADSORPTION.

Other Vapors and Gases. Other gases may also be condensed but the great affinity of the gels for water is a serious limitation on account of the difficulty of securing, industrially, gases which are free from water.[117] Condensation of petroleum vapors breathed from stor-
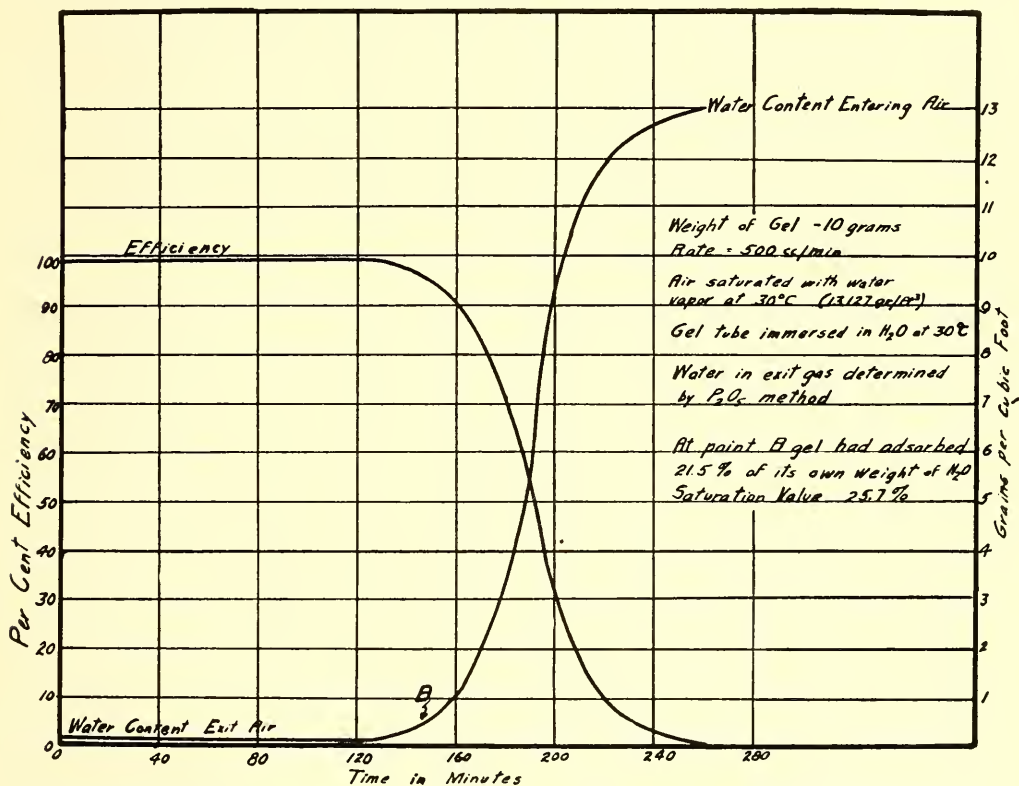
Fig. 182.—Adsorption of Aqueous Vapor by Silica Gel at 30°C.

age tanks or the reclamation of lacquer solvents from air would be useful and easy of accomplishment were it not for the fact that the gel shows a preferential action toward water as compared with hydrocarbon or other organic vapors.

Adsorption of SO_2 has been exhaustively studied by Patrick and his collaborators and a long list of condensible vapors has been experimented upon. This literature has been critically reviewed by Weiser [118]

[116] Truog, Emil, *Colloid Symposium Monograph,* **111,** 228-240 (1925).
[117] Teitsworth, Clark S., U. S. Pat. 1,570,537 (Jan. 19, 1926).
[118] Weiser, Harry B., "The Hydrous Oxides," 1st ed., New York: McGraw-Hill Book Co., Inc., **1926.**
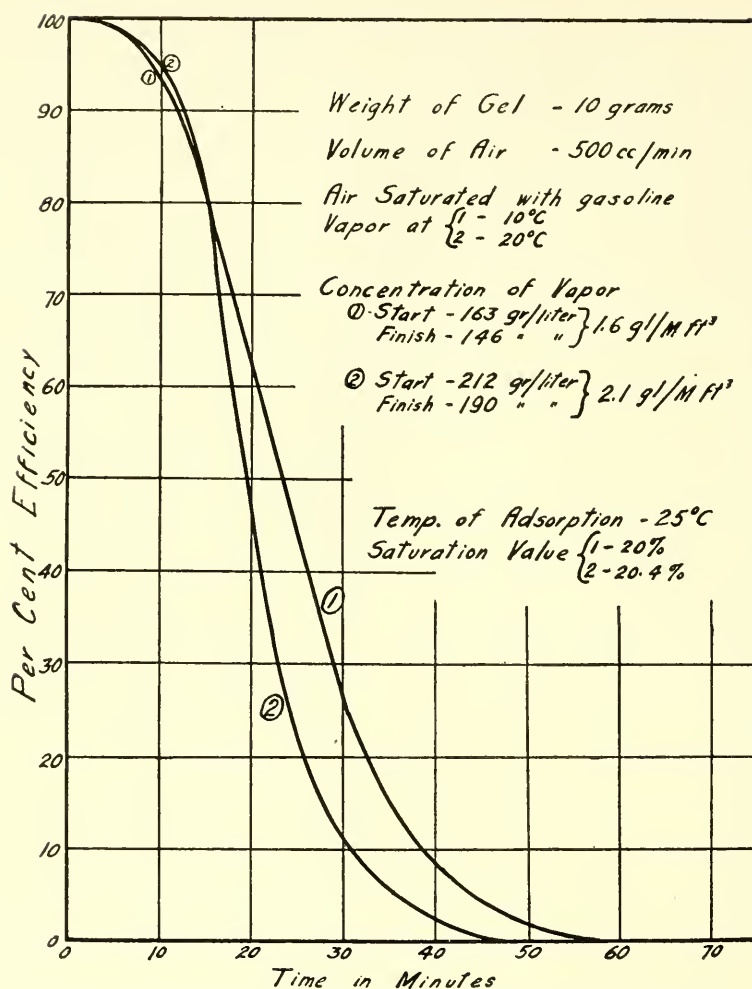
Fig. 183.—Adsorption of Gasoline Vapor by Silica Gel.

and is not extensively treated here as our principal concern is with the soluble silicates.

Sulfur Compounds.   Silica gel [119-129] is also used for adsorption

[119] Ray, Arthur B., *Chem. & Met. Eng.*, **29**, 354-359 (1923) ; *C. A.*, **17**, 3390.
[120] Gas Accumulator Co., Brit. Pat. 234,462 (May 22, 1924) ; *C. A.*, **20**, 804.
[121] Bradner, D. B., U. S. Pat. 1,457,493 (June 5, 1923) ; *Chem. & Met. Eng.*, **29**, 72 (1923).
[122] Miller, E. B., Am. Inst. Chem. Eng., 12th Semi-Annual Meeting, Montreal, Can. (June 28, **1928**) ; Davison Chem. Co. Bull. (Baltimore, Md.: Aug. **1920**).
[123] Holden, E. C., *Chem. & Met. Eng.*, **28**, 801-804 (1923) ; *C. A.*, **17**, 2333.
[124] Anon., *Chem. & Met. Eng.*, **29**, 121 (1923).
[125] Furness, Rex, *Chem. Ind.*, **42**, 850-854 (1923) ; *C. A.*, **17**, 3774-3775.
[126] Chaney, N. K., Arthur B. Ray, and A. St. John, *Ind. Eng. Chem.*, **15**, 1244-1255 (1923).
[127] Patrick, W. A., *Chem. & Met. Eng.*, **22**, 949-950 (1920).
[128] Behr, E., and W. Urban, *Z. angew. Chem.*, **36**, 57-60 (1923) ; *C. A.*, **17**, 1741-1742.
[129] *Silica Gel Corporation*, Baltimore, Md., No. 2 (1921).

of sulfur compounds in refining petroleum and benzol, from which processes it may be regenerated by displacement of adsorbed material with water and by heating. This method has the great advantage of leaving unattacked the valuable unsaturated compounds which are removed in refining with sulfuric acid.

References to the literature of preparation and use of silica gels including patents have been assembled by Kausch.[130]

Reactions in Gels. The physical form of silicious gels has been used to modify certain reactions by altering the rate at which the react-
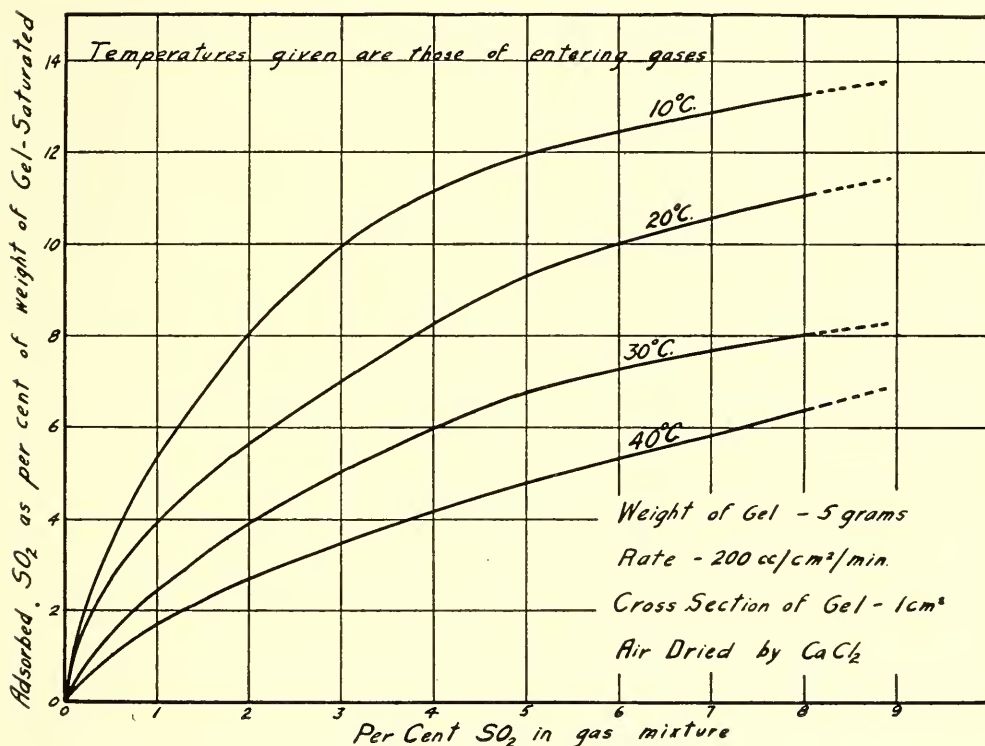
Fig. 184.—Adsorption of SO_2 by Silica Gel.

ing compounds come into contact. The beautiful experiments of Liesegang [131] and Holmes [132] are of this character. If a soluble iodide is mixed with a silicate solution which is then caused to gel by the addition of acid, a solution of a lead or mercuric salt may then be poured upon the surface of the solid gel. A slow process of diffusion brings the heavy metal and iodine into contact without agitation and large crys-

[130] Kausch, Oscar, "Das Kieselsäuregel und die Bleicherden," Berlin: Springer, 1927.

[131] Liesegang, *Z. anorg. Chem.*, **48**, 364 (1906); *Z. physik. Chem.*, **59**, 444 (1907).

[132] Holmes, Harry N., "Laboratory Manual of Colloid Chemistry," New York: John Wiley & Sons, Inc., 1922, 93; *J. Am. Chem. Soc.*, **40**, 1187-1195 (1918).

tals are formed, very different from the finely divided product of mixing the solutions directly. This method has been applied to the formation of lead trees, gold crystals, and the rhythmic bands which simulate the banding of agate. It would appear to be applicable to any cases in which a solid is formed by the interaction of two aqueous liquids, one of which is miscible with a silicate solution or a silica sol. The following procedure from Holmes gives the technic for one case:

"A 1.06 specific gravity waterglass—N acetic acid mixture, containing 2 cc. of N lead acetate to every 25 cc. was poured into test tubes. After the silicic acid gel set firmly, it was covered with 2 N potassium iodide. A compact layer of lead iodide quickly formed on the surface, followed very soon by crystallization below the surface of the gel. In a few days fern-like fronds grew down into the gel, mixed with many hexagonal plates. These concentrations may be varied with interesting results, and the lead salt may be used above the gel with the potassium iodide in the gel. The first order is much better."

BASE FOR CATALYSTS.

The great surface of silica gels makes them useful for reactions which take place on surfaces when it is possible to so activate the silica that it will function.[133] Platinized silica gel has been used for the catalytic conversion of SO_2 to SO_3 in the contact process for sulfuric acid. Other catalytic agents, as nickel for hydrogenating fatty oils, have been deposited on gel surfaces.[134-139]

BASE EXCHANGING GELS.

High Silica Silicates. Wheaton[140] found that by partly neutralizing a silicate solution with an acid under such conditions that a gel was formed, and washing out the salt of the acid, part of the sodium remained adsorbed or combined in such a way that it did not give an alkaline reaction to indicators. This sodium could be partly displaced

[133] *Silica Gel Corporation, Baltimore, Md., Bull.* No. 2, 29 (1921).
[134] Van Arsdel, Wallace B., U. S. Pat. 1,497,815 (June 17, 1924).
[135] Bosch, Carl, Otto Schmidt and Alwin Mittasch, U. S. Pat. 1,391,666 (Sept. 27, 1921).
[136] Patrick, Walter A., Brit. Pats. 212,034 and 212,035 (Jan. 17, 1923).
[137] Patrick, Walter A., U. S. Pats. 1,297,724 (March 18, 1919); 1,577,187, 1,577,188, 1,577,189, 1,577,190 (March 16, 1926).
[138] Reyerson, L. H., and Thomas Kirk, *Colloid Symposium Monograph,* Vol. 3, 1925, 1, p. 99-102.
[139] Reyerson, L. H., and L. E. Swearingen, *J. Phys. Chem.,* 31, 88-101 (1927); *C. A.,* 21, 844.
[140] Wheaton, H. J., U. S. Pat. 1,100,803 (June 23, 1914).

by equivalent quantities of calcium or magnesium from hard water. The exchange would also proceed in the reverse direction when the exhausted gel was brought into contact with a sodium salt solution. Thus the material could be used like a zeolite to soften water and could be regenerated with common salt. This gel did not reach great practical importance on account of relatively low capacity as compared with other available base-exchanging compounds.

"Doucil." * A material of similar structure and much greater capacity was obtained by forming a gel of the composition of Na_2O, $Al_2O_3,5SiO_2$. With this an exchange of more than 6 per cent of its weight of CaO could be obtained, a higher capacity than either natural or prior synthetic materials would yield. It is known as Doucil.[141-145]

The porosity of this gel is such that the grains after centrifugal extraction contain approximately their own weight of water. When air dried, the grains become opaque. If they are then put into water a transparent area is seen to form at the outer surface and progress rapidly inward from all directions. The pressure of the rush of water through the capillaries is enough to disrupt the grains by the pressure of entrapped air, which may be seen to escape as bubbles when the grains burst.

As grain size is an important consideration in water-softening plants

* Doucil, manufactured by the American Doucil Company, 121 South Third Street, Philadelphia.

[141] Vail, James G., *Trans. Am. Inst. Chem. Eng.,* **16**, Pt. 2, 119-131 (1924); *Silicate P's & Q's,* **4**, No. 5; **5**, No. 7, Philadelphia: Philadelphia Quartz Co., **1925; 6**, No. 5, No. 10 **(1926).**

[142] Joseph Crosfield & Sons, Warrington, England, Booklet, "Water softening by means of Doucil."

[143] Hilditch, T. P., and H. J. Wheaton, *Chem. & Ind.,* **44**, No. 36, 885-887 (1925).

[144] Joseph Crosfield & Sons, and H. J. Wheaton, Brit. Pat. 142,974 (May 20, 1920); Mex. Pat. 21,986 (Nov. 5, 1922); Brit. Pat. 196,646 (April 30, 1923); Fr. Pat. 565,006 (Nov. 2, 1923); Belg. Pat. 309,780 (May, 1923); Brit. Pat. 177,746 (April 6, 1922); Belg. Pat. 301,994 (April 15, 1922); Fr. Pat. 549,051 (Mar. 17, 1922); Mex. Pat. 21,987 (Nov. 5, 1922); Brit. Pat. 206,267 (Nov. 8, 1923); Belg. Pat. 312,583 (Sept. 8, 1923); Fr. Pat. 569,677 (Jan. 9, 1924); Mex. Pat. 21,989 (Nov. 5, 1922); Ger. App. No. C. 33879 Class IV/12 i.

[145] Hilditch, Wheaton, and Crosfield, Brit. Pat. 206,268 (Nov. 8, 1923); Belg. Pat. 312,522 (Sept. 8, 1923); Fr. Pat. 569,725 (Jan. 9, 1924); Ger. App. 33,877 (Class VIII/21); Brit. Pat. 203,158 (Sept. 6, 1923); Belg. Pat. 312,584 (Sept. 8, 1923); Fr. Pat. 569,698 (Jan. 1924); Mex. Pat. 21,990 (Nov. 3, 1922); Ger. Appl. 33,878 (Class IV/12i); Brit. Pat. 206, 269 (Nov. 8, 1923); Belg. Pat. 312,523 (Sept. 8, 1923); Fr. Pat. 569,726 (Jan. 1924); Ger. Appl. 33,876 (Class VIII/21); Brit. Pat. 203,497 (Sept. 13, 1923); Fr. Pat. 565,226 (Nov. 5, 1923); Belg. Pat. 309,963 (May 1923); Ger. App. C.33613 (Class IV/85 b2); Brit. Pat. 212,453 (March 13, 1924); Brit. Pat. 224,656 (Nov. 20, 1924); Brit. Pat. Prov. Specification 28,773 (1924); U. S. Pat. 1,586,764 (June 1, 1926).

it is convenient to bring the gel on the market with its pores full of water and to avoid allowing it to dry before it is put in service.

It is neutral to indicators and capable of thousands of cycles of soften-
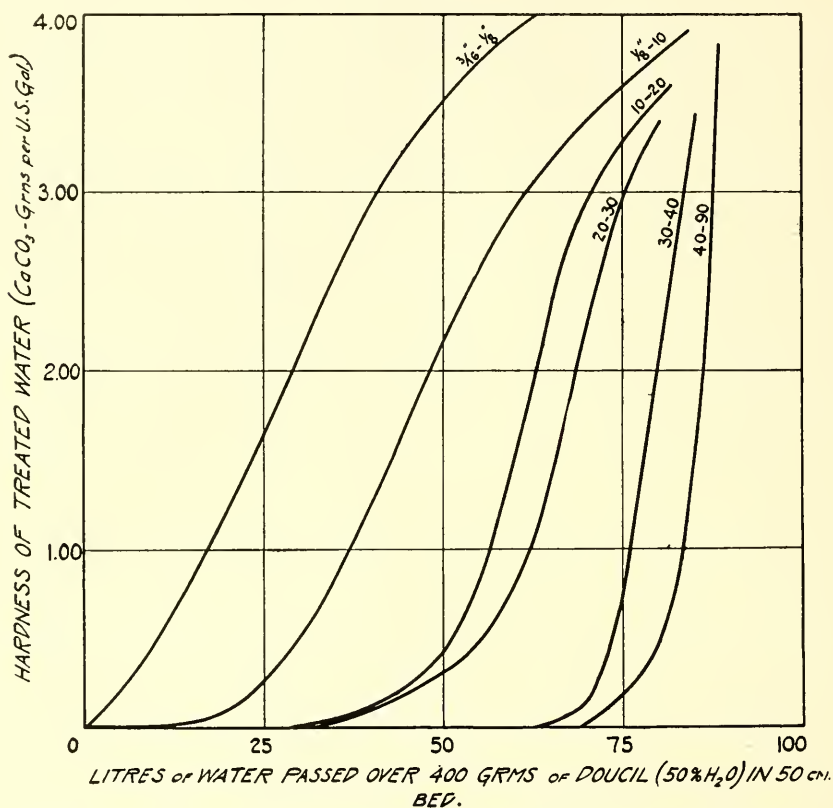
FIG. 185.—Water Softening by Doucil of Varying Grain Size.

ing and regeneration. Its rated capacity is 12,500 grains CaCO₃ per cubic foot (1 cu. ft. = 50 lbs. containing 50% water) for a product graded between 8 and 30 mesh, producing water of zero hardness.

Chapter XII.

Additional Uses.

Our earlier chapters have dealt with uses of soluble silicates in a sequence intended to illustrate the properties involved, and we arrive at the final group with many things unsaid. If the elements of this chapter seem rather miscellaneous, the reader is asked to view them as suggestions, for the examples have been chosen with a view toward helping him realize the diversity of properties of soluble silicates which stand at the service of industry. There can be little doubt that new uses will be found as new problems are presented and though many of these have little industrial importance, a patient cultivation of the field is sure to yield some good fruit.

Purifying Water.

Precipitation of Silicate Solution by Sodium Compounds.

Since the introduction of fusion methods for making silicates which have the ability to exchange bases, as do zeolites, various workers have sought to reach the same results by wet methods. The most important of these products are sodium aluminum silicates, for which the aluminum may be derived from various soluble compounds, but all the wet processes make use of a silicate solution.[1, 2, 3, 4]

Boehringer and Gessler[5] precipitated silicate solutions with sodium aluminates, plumbates, zincates and stannates, collected the flaky precipitates, and by filtering and by drying made granular masses capable of removing alkaline earth metals as they occur in natural waters.

Characteristics of These Precipitates. These could be regenerated by contact with salt solutions according to the equation:

$$Ca(R_2O_3)_x . (SiO_2)_y + 2NaCl = Na_2(R_2O_3)_x . (SiO_2)_y + CaCl_2$$
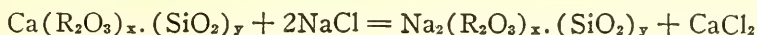
[1] Killeffer, D. H., *Ind. Eng. Chem.*, 15, 915-917 (1923); *C. A.*, 17, 3393.
[2] Gans, R., *Chemische Industrie*, 32, 197-200 (1909); U. S. Pat. 943,535 (1909); Can. Pat. 208,968 (March 1, 1921); *C. A.*, 15, 1195; Ger. Pats. 423,224 (Nov. 18, 1916); 426,083 (Oct. 12, 1919).
[3] Vogtherr, H., *Z. angew. Chem.*, 33, 1, 241-243.
[4] Gutensohn, A., U. S. Pat. 773,494 (Oct. 25, 1904); *J. Soc. Chem.*, 23, 1109.
[5] Boehringer, Rudolph, and Albert E. Gessler, U. S. Pat. 1,050,204 (Jan. 14, 1913).

in which the value of x and y might vary widely. Indeed, they could be used in general for all the purposes proposed by Gans, but with the advantage of higher rates of reaction, at least partly due to greater porosity and more surface of the insoluble silicate exposed to the water or salt solution.

Bodies known to have properties similar to zeolites had been previously made experimentally by precipitating silicate solutions. Thus Way,[6] studying the action of soils toward fertilizing materials, attempted the synthesis of compounds which might occur in the soil and observed the exchange of bases by double silicates made by precipitating silicate solutions but did not discover that the exchange reaction could be reversed; and Haushofer [7] described the preparation of sundry double silicates by the use of various salts for precipitation. Similar products were also encountered in trying to duplicate in the laboratory zeolitic minerals which occur in nature,[8, 9, 10, 11] but not until after the teachings of Gans did they assume any industrial importance.

Bibliography of Zeolite Water Softening.* The technic of wet methods directed to economies and particularly to the development of silicates able to exchange increasing amounts of bases without losing their hard granular character on long exposure to water and adapting them to various reactions has claimed the attention of numerous inventors, of whom Wheaton, Hilditch, and Behrman, who made use of the peculiar characteristics of gel structure, have been mentioned in the foregoing chapter.[12-19]

TREATMENT OF GREENSAND BY SILICATE SOLUTIONS.

Silicate solutions have also been employed in preparing glauconite or natural greensand for use as a water softener. In its natural state

[6] *J. Roy. Agri. Soc.*, **13**, 128-133 (1852).
[7] *J. prakt. Chem.*, **99**, 241 (1866).
[8] Ammon, von, "Silikate der Alkalien u. Erden" (Göttingen, **1862**), 37; *Gmelin-Kraut*, **3**, 1,280 (1912).
[9] Heldt, *J. prakt. Chem.*, **94**, 143 (1865).
[10] Deville, *Compt. rend.*, **54**, 324-327 (1862).
[11] Lemberg, *Z. deut. geol. Ges.*, **35**, 573 (1883).
[12] De Brünn, P., U. S. Pat. 1,161,200 (Nov. 23, 1915); Can. Pat. 204,243 (Sept. 21, 1920); *C. A.*, **14**, 3290; Brit. Pat. 26,078 (Nov. 13, 1913); *C. A.*, **16**, 603.
[13] Kolb, A., U. S. Pat. 1,193,794 (Aug. 8, 1916).
[14] Kriegsheim, H., U. S. Pat. 1,208,797 (Dec. 19, 1916).
[15] Rudorf, G., U. S. Pat. 1,304,206 (May 20, 1919).
[16] Massatsch, C., U. S. Pat. 1,343,927 (June 1, 1920).
[17] Willcox, O. W., U. S. Pat. 1,499,492 (July 1, 1924).
[18] Behrman, A. S., U. S. Pat. 1,515,007 (Nov. 11, 1924).
[19] Blumenthal, F., U. S. Pat. 531,836 (March 31, 1926).
* A bibliography of the extensive literature of zeolite water softening prepared by Bartow and Baker has not been published, but a copy is in possession of the Philadelphia Quartz Company.

it tends to undergo partial decomposition at surfaces long exposed to water, which is thus contaminated and discolored by iron compounds, a very objectionable characteristic in a device whose function is to provide a supply of clear soft water. To overcome this, Lee treated glauconite grains with $Al_2(SO_4)_3$ in a 10°Baumé solution, washed, treated with a 10°Baumé silicate solution (presumably $Na_2O, 3.3SiO_2$), washed again to neutral reaction and then baked at 500°C., which yielded a stable hard product in which iron at the surface was oxidized from its original green color to dark brown.[20, 21]

This procedure was simplified by Nordell,[22] who found it sufficient to exhaust the glauconite with hard water, that is, to replace the exchangeable alkali metals with alkaline earth metals, and then to apply a hot silicate solution. The glauconite was thus stabilized without change of color and more cheaply. The finished product should be kept moist, for, in common with all wet-process base-exchange materials, it undergoes some loss of exchange power if completely dehydrated.[23] The capacity of greensand may be increased as much as 50 per cent by soaking in hot dilute $Na_2O, 3.3SiO_2$ without previous exchange of alkali metal for alkaline earth metal. During this treatment silica is deposited in the grains,[24] tending to harden them; but the reason for increased exchange capacity is not fully understood. The effect has also been observed on base-exchange silicates made by sintering argillaceous materials with alkaline compounds.

MISCELLANEOUS USES.

PURIFYING SUGAR SOLUTIONS.

Colloidal compounds which contain silica have long been known to have value for separating gums and coloring matter from sugar solutions. Aluminum hydroxide and silicate of soda were used by Clough. Bachler [25] attributed the action to the fact that the gums are colloids of negative charge capable of precipitation by a positively charged colloid. Neutralization of acids is also necessary to satisfactory recovery of

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[20] Lee, Yong K., U. S. Pat. 1,527,199 (Feb. 24, 1925).

[21] Brit. Pat. 228,380 (March 17, 1924). See also U. S. Pat. 1,472,011 (Oct. 23, 1923).

[22] U. S. Pat. 1,506,198 (Aug. 26, 1924).

[23] See also Permutit Company, Brit. Pat. 228,380 (March 17, 1924); *C. A.,* **19,** 2866 (1926).

[24] Béhrman, A. S., International Filter Co., Tech. Bulletin No. 3002, U. S. Pat. 1,624,711 (April 12, 1927).

[25] Bachler, F. R., Aus. Pat. 471,295 (1914); *Cf.* Wells, C. H., *Louisiana Planter and Sugar Mfg.,* **71,** 394 (1923).

sugar.[26-30] The silicious colloid may not always be produced from a silicate solution but such is a convenient starting point.

Prevention of Fungus Growths.

The fungi which cause blue stain on freshly cut lumber in hot, humid climates can be prevented by passing the freshly cut boards through a dilute silicate bath, which has the advantage over other alkaline salts that it penetrates the wood less deeply. It has been successfully used on a large scale.

Experiments to use silicate solutions as sealing media in tree grafting gave a much lower percentage of success than when waxes were employed. This was to be expected.

Insecticides.

Insecticides in which silicate solutions exert a deflocculating or adhesive action have been used.[31] They are not of themselves used to destroy insect life without injury to plants, but are able to help the adherence of sulfur or other more active materials. Good dispersion of insecticides is also important to secure covering of plant surfaces, and here the deflocculating properties of silicates come into play. Sticky silicate solutions have been used to fill trenches for the prevention of the migration of corn borers.

Leather Tanning.

Processes for preparing leather are grouped into vegetable and mineral tannages. The deposition of basic chromium compounds is the most familiar of the second group, but it is well known that a great many inorganic compounds may be used to prepare skins in a non-putrescible condition more or less suited to the various uses of leather. Silica in colloidal dispersion has been studied in this connection and the development has reached a point where flexible white leathers made with its help are now in commercial use. Sols containing up to five per cent silica are stabilized with mineral acids at a pH of about 2.5, in which condition they may be mixed with various salts such as alum, barium chloride, magnesium sulfate, chromium sulfate, ferric chloride, etc., without gelling.

[26] Clough, W., U. S. Pat. 87,759 (1869).
[27] Wells, C. H., *Louisiana Planter and Sugar Mfg.*, **71**, No. 21, 394 (1923).
[28] Deguide, C., U. S. Pat. 1,579,090 (March 30, 1926).
[29] Kullgren, C. F., U. S. Pat. 1,616,131 (Feb. 1, 1927).
[30] Urban, Karel, U. S. Pat. 1,577,389 (Mar. 16, 1926).
[31] Howard, H., U. S. Pat. 1,583,154 (May 4, 1926).

Such a sol may be made by diluting a 40°Baumé solution Na_2O, $3.3SiO_2$ with 3 to 4 parts water and after thorough mixing, pouring it with constant stirring into an excess of hydrochloric or sulfuric acid so diluted that the residual acidity is about decinormal, with a pH of 2.5. The silica sol alone, which would yield leathers containing up to 20 per cent silica, was of no use because the leather was too weak and brittle—the present commercial process involves the use of metallic salts with the sol and yields a white washable leather of good strength and great pliability.[32-36]

Silicate solutions can also be used as neutralizing agents in chrome tanning. The hides are treated after removal from the tanning baths to reduce the acidity of the salt adsorbed on the fiber and also to neutralize the residues of acid liquor held mechanically in the pores. The exact control of the process to prevent danger to the leather, which would result from any excess of a stronger alkali, is readily accomplished with silicate solutions.

RAYON.

Rayon, formed by extruding viscous solutions of cellulose into a bath which coagulates the liquids to produce threads for a wide variety of textile uses, has of late years assumed great technical importance. The viscose process, which depends upon the formation of a xanthogenate by the action of sodium hydroxide and carbon disulfide upon cellulose, is one of the most important. The coagulating bath first used for this process was made from acid salts, notably bisulfites; but it was found that the threads after leaving such a bath could be passed through a silicate bath with the result that they had less tendency to stick together.[37, 38] It has also been proposed to add silicate solutions to the sodium hydroxide used in preparing the viscose colloid, the purpose being to obtain a stiffer fiber adapted to the imitation of horsehair and other special uses, such as fabric for Welsbach mantles.[39]

Further study by Cross, however, revealed the fact that silicate solutions, particularly those of relatively high silica content, are well adapted to cause the original coagulation of the viscose. For example,

[32] Société Genty, Hough et Cie., Ger. Pat. 322,166 (Aug. 8, 1918).
[33] Hough, A. T., personal communication.
[34] Le Cuir, "Le Tannage à la Silice" (Paris, Aug., Sept., Oct., **1919**).
[35] See also Morin, H., U. S. Pat. 1,404,633 (Jan. 24, 1922).
[36] Röhm, O., U. S. Pat. 1,397,387 (Nov. 15, 1921); U. S. Pat. 1,569,578 (Jan. 12, 1926).
[37] Howorth, T. E., Brit. Pat. 8,045 (1906).
[38] F. C. S., Fr. Pat. 361,319 (1906).
[39] Huber, Joseph, and Paul Eckert, Ger. Pat. 405,601 (Nov. 8, 1924).

"the viscose is projected into a solution containing twenty per cent by weight of a silicate of soda of the composition $2Na_2O,7SiO_2$, and maintained at a temperature of from 40° to 50°C. This bath, although strongly alkaline in the ordinary sense, has the property of coagulating the viscose to the solid form, and this, after fixation (for instance, by 1 per cent sulfuric acid) and after any other requisite, or desirable, manipulation, or treatment, results in lustrous threads, filaments and the like, of excellent quality." [40, 41]

ELECTROLYTE IN STORAGE BATTERY.

It has been proposed to use a mixture of sodium metasilicate and sodium hydroxide as electrolyte in a storage battery with nickel and iron electrodes. This electrolyte has the advantage over sodium hydroxide that it does not "creep," and is much cheaper than potassium hydroxide, which is ordinarily used to avoid this defect. Although the liquid is more viscous than the pure hydroxide solutions and hence less liable to splash, this process is not to be confused with the use of gels in acid electrolytes, as the silica remains in solution. By choosing silicates of high purity no detrimental compounds need be introduced into the alkaline electrolytes.[42]

DEHYDRATING STEATITE.

In the removal of water from steatite by electro-osmosis the addition of soluble silicates favorably influences the process. This is probably a combined action of colloid and electrolyte, and the material is held dispersed and made amenable to the influence of the current.[43]

STRAW PAPER FOR CORRUGATING.

It has been proposed to use the solvent action of silicate solutions for reducing straw to a pulp suitable for making the sort of paper required by the maker of corrugated paper for shipping containers. The fibers are sufficiently separated by cooking in the silicate solution to permit preparing them for the paper machine by a short beating operation, after which the silicate together with organic materials which it has dissolved are precipitated in the fiber with aluminum sulfate or other convenient precipitant.[44, 45]   Thus the cooking reagent becomes

[40] Cross, C. F., U. S. Pat. 1,538,689 (May 19, 1925).
[41] Courtaulds, Ltd., London, Ger. Pat. 411,167 (March 24, 1925).
[42] Freeth, F. A., and L. A. Munro, U. S. Pat. 1,541,699 (June 9, 1925).
[43] Schwerin, B., U. S. Pat. 1,266,330 (May 14, 1918).
[44] Dixon, U. S. Pat. 52,545 (1866).
[45] Cobley, T. H., Brit. Pat. 13,096 (1896).

a sizing material and the problem of the factory effluent, which is a serious one in making straw paper with lime, is simplified. The silicate could be used in combination with other alkaline reagents, and for kinds of fiber other than the straw which was investigated.[46]

CLARIFICATION OF WASTE WATERS.

A similar double use of a silicate reagent has been suggested for controlling the character of a laundry effluent. Silicate used as a detergent can be precipitated in the waste waters which it helps to clarify for disposal.

REMOVAL OF FLUORINE FROM PHOSPHORIC ACID.

A special use of silicate solutions is for removing fluorine from phosphoric acid made by smelting natural phosphate rock with sand and coke. Fluorides are always present in the raw material but can be precipitated as sodium silico-fluorides. A silicious type of silicate is to be preferred for this use, but it should be used dilute to avoid gel formation. Na_2O, $3.3SiO_2$ is satisfactory. Ten thousand pounds of acid at 1.70 specific gravity are treated with 20 pounds of commercial 1.38 specific gravity (40°Baumé) silicate in 20 gallons of water, allowed to settle, and then filtered through sand. The fluorine is reduced from about 0.2 per cent to 0.02 per cent.[47]

EXTRACTION OF VANADIUM AND RADIUM.

Silicate solutions have been used to react with calcium fluoride and hydrochloric acid to make, with sodium nitrate, a reagent for the extraction of vanadium and radium from carnotite ores. The vanadium and radium values can be extracted from 2000 pounds of dried residue of an alkaline digestion of carnotite ores by heating for one hour at not more than 3000°F., with the following reagents: [48]

Hydrochloric acid (12°Baumé)	4000 pounds
Calcium fluoride (fluorspar)	200 "
Sodium silicate	25 "
Sodium nitrate	42 "

PHYSIOLOGICAL EFFECTS OF SILICATE SOLUTIONS.

THERAPEUTIC USES.

Effect in Potable Waters. In potable waters, silica is regarded as inert; and silicate solutions used for the control of corrosion in public

[46] Dedrick, C. H., U. S. Pat. 1,682,834 (Sept. 4, 1928).
[47] Carothers, J. N., and A. B. Gerber, U. S. Pat. 1,487,205 (March 18, 1924).
[48] Bleeker, W. F., U. S. Pat. 1,445,660 (Feb. 20, 1923).

supplies on a large scale, though not above a concentration of ten parts of silica per million, have produced no ill effects.[49]   The suspicion that silica in water might have something to do with cancer was investigated by comparing the cancer death rates in communities served with high and low silica waters.   The result was completely negative.   The death rate from cancer was slightly lower in the communities supplied by waters high in silica, though the differences were too small to be of any significance.[50]

Treatment for Tuberculosis.   Therapeutic use of silicate solutions and colloidal silica has been studied for the treatment of tuberculosis, arterio-sclerosis, asthma, and some other diseases.[51-65]   Silica is regularly ingested as part of the mineral content of cereal and other foods. Plants alleged to be of use in the treatment of tuberculosis contain large amounts of silica; animal experiments indicate that the silica content of the pancreas is subnormal with tuberculosis, and doses up to 10 mg. per day given intravenously are tolerated by man.   Large doses are definitely harmful.   By mouth 1 to 3 grams daily have been given in treating arterio-sclerosis.   There is a lack of exact information as to ratios used, and the results are not known to be important.

Buffer Solutions in the Treatment of Intestinal Diseases.   More recently Hepburn and Eberhard [66, 67] have studied the use of buffer solutions in the treatment of intestinal diseases and found them useful. Sodium metasilicate exhibited a much greater alkali reserve than a citrate buffer of similar pH and was able to neutralize much larger amounts of certain organic acids which are products of fermentation. Four-tenths normal sodium metasilicate, pH 12.56, and citrate buffer,

[49] Thresh and Beale, "Examination of Waters and Water Supplies," 3rd ed., Philadelphia: Blakiston, **1925**, p. 153.
[50] Thresh, *The Medical Officer* (Nov., 1923).
[51] Kühn, A., *Fortschritte Med.*, **41**, 75-7 (1923) ; *C. A.,* **17**, 3369.
[52] Scheffler, L., A. Sartory, and P. Pellisaier, *Compt. rend.,* **171**, 416-8 (1920) ; *C. A.,* **14**, 3725.
[53] Messner, J., *Pharm. Monatshefte,* **3**, 82-3 (1922) ; *C. A.,* **16**, 3972.
[54] Luithlen, F., *Wiener klin. Wochschr.,* **35**, 349 (1922) ; *C. A.,* **17**, 434.
[55] Kühn, A., *Mediz. Klin.,* **18**, 9-11 (1922) ; *C. A.,* **16**, 2934.
[56] Kühn, A., *Z. Tuberk.,* **32**, 320 (1922) ; *C. A.,* **16**, 2934.
[57] Kahle, Hanns, *Beitr. klin. Tuberk.,* **47**, 296-324 (1921) ; *C. A.,* **16**, 1616.
[58] Schubauer, F., *Biochem. Z.,* **108**, 304-8 (1920) ; *C. A.,* **15**, 269.
[59] Gye, W. E., and W. J. Purdy, *Brit. J. Exptl. Pathol.,* **3**, 75-85, 86-94 (1922).
[60] Peter, B., *Pharm. Monatshefte,* **4**, 63-7 (1923) ; *C. A.,* **17**, 2629.
[61] Gaube, "Cours de mineralogie biologique" (1904).
[62] Olivier, Decene, "Les Silicates en Therapeutique" (1906).
[63] Scheffler, *Arch. gen. méd.* (June 1908).
[64] Robin, Albert, "Therapeutique usuelle traitement de la tuberculose" (1912).
[65] Rudsit, K., *Folia Haematol.,* **33**, 95-104 (1924) ; *C. A.,* **21**, 959.
[66] Hepburn, Joseph, and H. M. Eberhard, *Am. J. Med. Sci.,* **166**, 244 (1923).
[67] Hepburn, Joseph, *J. Am. Dietetic Assoc.,* **1**, 55-59 (1925).

pH 12.36, were titrated with 0.2 normal acid with phenol red to a pH of 7, with the following results:

TABLE 123. *Cubic Centimeters of 0.2 Normal Acid Required to Produce a pH of 7.0.*

Acid	With 100 cc. of Sodium Metasilicate Solution	With 100 cc. of Citrate Buffer Solution
Hydrochloric	174.44	7.09
Acetic	179.80	7.34
Butyric	180.84	7.29
Lactic	182.87	7.51

Silicate Solutions for Surgical Bandages. Silicate solutions for making light rigid surgical bandages have been long and favorably known. The fabric is saturated with an adhesive silicate, preferably $Na_2O, 3.3SiO_2$, diluted just enough to penetrate, and bound on over a cotton dressing. It dries in a few hours to a greater strength than gypsum plaster and it is lighter and less bulky.

ACCIDENTAL DOSES.

Silicate in the Eyes. The accident of splashing strong silicate solutions, such as are used for adhesive purposes, into a human eye is a painful experience. The effect is much less deleterious than that of caustic solutions of like alkali content. The discomfort is due not only to the alkali but to the precipitation of granular material in the eye. The presence of the silica, on the other hand, mitigates the action of the alkali on the tissue; and in no known case has the injury caused by a silicate solution lasted more than a few days.

Like other accidents, it should be dealt with before it takes place. The wearing of glasses is a simple and effective precaution. Emergency treatment consists in thorough washing with warm water, preferably holding the afflicted eye in a gentle stream and getting circulation under the lids till most of the silicate has been removed, remembering that more water is required than one would naturally expect. This should be followed by liberal application of boric acid solution and the inspection of a physician. In some plants it is the practice to put a drop of castor oil in the eye, but the other method has been observed in a large number of cases without a case of permanent injury, though in the worst cases two or three days of severe inflammation and discomfort are often experienced.

Silicate on the Hands. Complaints sometimes arise from workers who get silicate more or less continuously on their hands. This can be

avoided by the use of rubber gloves. The effect on the skin of an adhesive silicate in concentrated form is first to cause chapping, as would be the case if the hands had a similar exposure to laundry soap or other materials of like alkalinity.

Silicate like other alkalies tends to remove the natural oils which have an emollient effect on the skin, and if in addition a thick film is allowed to dry it adheres and shrinks, tending to tear the epidermis from the dermis. Another effect is mechanical irritation due to hard sharp-edged films of silicate which form on the hands as the solution dries. The combined effect of alkalinity and abrasion may become very unpleasant. Greasing the hands and keeping them clean are useful measures. Cases of infection are due to outside contamination, as the silicate solutions supplied by the makers are sterile; they have indeed been recommended as antiseptics.[68, 69]

Silicate Taken by Mouth. Small amounts of silicate solutions which may be accidentally taken by mouth are negligible; their rather unpleasant taste is usually sufficient to guard against such mishap. They have even been used internally to neutralize acidity in place of bicarbonate of soda taken by mouth. Two hundred cubic centimeters of a strong solution for egg preserving when taken internally induced violent physical distress, but did not prove fatal.[70]

It is hoped that the foregoing pages have made plain that silicates of soda, rightly used, are capable of many services of substantial value, but just as plowshares and pruning hooks can be fashioned into implements of destruction, so silicates of soda are capable of wrong use which a knowledge of their nature provides the means to avoid.

[68] Picot, *Compt, rend.,* **75,** 1516-1519, 1124-1125 (1872) ; **76,** 99-103 (1873) ; Abst. in *Chem. News,* **27,** 46 (1873).
[69] Champouillon, *Compt. rend.,* **76,** 355-356 (1873) ; Abst. in *Chem. News,* **27,** 94-96.
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